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The effect of surface active agents on the rate of absorption of carbon dioxide by water

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Abstract—Carbon dioxide was absorbed into water containing surface-active agents and running in a thin film over a sphere.

The results are compared with theoretical calculations based on the assumption of equilibrium at the interface, absorption being controlled by diffusion. The comparison indicates that at a certain concentration of the commercial agents there is a resistance to absorption which falls to zero at very low and at very high concentrations. With a chemically pure agent, there is no resistance to absorption, other than that due to diffusion, so that theory and experiment agree. With a solution containing the same pure agent plus a small amount of impurity, the behaviour is similar to that of the commercial agents.

These results indicate that surface-active agents can reduce the absorption up to 25% in a system in which they do not influence the hydrodynamics.

Résumé—De l'anhydride carbonique est absorbé par de l'eau contenant des agents tensio-actifs, s'écoulant en couche mince sur une sphère.

Les auteurs comparent les résultats obtenus avec les calculs théoriques basés sur l'hypothèse d'équilibre à l'interface, la diffusion contrôlant l'absorption. La comparaison montre que pour une certaine concentration des agents commerciaux, il se produit une résistance à l'absorption qui tombe à zéro pour des concentrations très faibles ou très élevées.

Avec un agent chimiquement pur, il n'y a, comme résistance à l'absorption, que celle inhérente à la diffusion, ce qui explique l'accord entre la théorie et l'expérience. Une solution contenant lè même agent pur, avec une petite quantité d'impuretés, se comporte comme les agents commerciaux.

Ces résultats montrent que les agents tensio-actifs peuvent réduire l'absorption jusqu 'à 25% dans un système où ils n'influencent pas l'hydrodynamique.

INTRODUCTION

THE effect of surface active agents on such properties of an interface as the surface tension is well known, but their influence on the rate of mass transfer across an interface is uncertain. This uncertainty is due to the fact that mass-transfer experiments are usually carried out on moving systems, and the addition of surface-active agents may alter the hydrodynamics, an effect which is difficult to separate from a surface resistance.

In liquid-liquid systems, two methods have been used. In the first of these, the effect on the rate of mass transfer to or from a drop, which is rising or falling through a stagnant liquid, is measured. GARNER and his co-workers [1, 2] have used this method and concluded that surface active agents present a resistance to mass transfer. LINDLAND and TERJESEN [3] came to a similar conclusion and developed a theory for the resistance on the basis that it is proportional to the interfacial concentration of surface-active molecules. The second method is to measure the transfer rate across an interface between stirred

liquids. HUTCHINSON [4] concluded from this type of experiment that sodium cetyl sulphate caused an interfacial resistance, the magnitude of which was dependent on the diffusing molecules. HOLM and TERJESEN [5] found a minimum in the transfer rate and concluded that the rise after the minimum was due to an increased interfacial area. An excellent review of earlier work on these two methods and on the effect of surface films on evaporation is given in reference [1].

The data in the literature on the effect of surface active agents on the rate of absorption of gases by liquids is not so extensive. TERNOVSKAYA and BELOPOLSKII [6] studied the effect of three sulphonate surface-active agents on the rate of absorption of sulphur dioxide in water flowing down a wetted-wall column. With increasing concentration of one of the agents, whilst the surface tension decreased, the HTU increased at first, and then fell off after reaching a maximum at a certain concentration. The effect of the second agent was similar but less pronounced, while the third caused an increase in HTU up to a constant value. These effects were said to be due to the adsorption layer at the interface modifying the hydrodynamics [7, 8, 9]. EMMERT and PIGFORD [10] compared the theoretical and experimental rates of absorption and desorption, for oxygen and carbon dioxide, in water which contained a sulphonate surface-active agent, and which flowed in laminar motion down a wetted-wall column. They concluded that there is an interfacial resistance, due to lack of equilibrium at the interface, even with pure water, and that the sole effect of the agent is to eliminate rippling. Subsequent work done by the present authors [11, 12] suggests that equilibrium does exist at the surface of pure water, and that the discrepancy between the theoretical and observed results obtained by EMMERT and PIGFORD is due to an interfacial resistance caused by the surface-active agent.

EXPERIMENTAL

In the present investigation, a modified form of wetted wall column has been used. This column, which utilizes water flowing over a sphere instead of down a cylinder, has been described in detail elsewhere [11].

The absorption gas used was carbon dioxide, produced at a purity greater than 99·8% from the solid. Air-free distilled water, with varying concentrations of surface-active agents, was used as the absorbing liquid and its temperature was maintained at 25·0 ± 1°C. The whole apparatus was enclosed in a constant-temperature room which was kept at 25·0 ± 0·5°C. During an experiment the carbon dioxide was drawn in from an atmospheric balloon through a rotameter which measured the rate of absorption. The column was purged at frequent intervals to prevent the buildup of impurities.

Four commercial surface-active agents were used, together with a specially prepared sample of one of them. These were :

(1) Teepol – An aqueous solution containing 21% active secondary alkyl sulphate with average molecular weight of 305, and a specific gravity of 1·075 at 25°C.

(2) Petrowet R – An aqueous solution containing approximately 33% of saturated hydrocarbon sulphate with an average molecular weight of 280 and a specific gravity of 1·067 at 21·5°C.

(3) Lissapol N – An aqueous solution containing 26·5% of ethylene oxide condensates of an average molecular weight of 638, and a specific gravity of 1·024 at 21·5°C [13].

(4) Sodium dodecyl sulphate – A solid commercial product of BP purity.

A specially pure sample of sodium dodecyl sulphate was prepared from homologue-free dodecyl alcohol. The alcohol was sulphated with chlorosulphonic acid in the presence of acetic acid at 0°C; after neutralizing with sodium carbonate, the sulphate was extracted with butanol, and after evaporation, crystallized. The crystals were thoroughly dried and were extracted with ether in a Soxlet for 16 hours. The product was then crystallized from ethanol and carefully dried.

For the liquid agents, solutions were made

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up to a known volume percentage and all concentrations referred to in this paper are with reference to the material as supplied and *not* to the active component. For the solid agents, solutions were made up to a known weight percentage of the material as supplied or made.

For ease of comparison, all experimental absorption rates were corrected to a partial pressure of carbon dioxide of 760 mm and to a water temperature of 25°C. The procedure for doing this is given in reference [11] and the maximum total correction needed in this work was under 3%.

To characterize the solutions, measurements were made of the surface tension and equivalent conductivity over the concentration range required. The surface tensions were determined using the drop weight method, with the corrections of HARKINS and BROWN [14]. The electrical conductivity was measured using a Mullard conductance bridge and a conductivity cell. The conductivity of the agent was found by subtracting the conductivity of the distilled water (about 3×10^{-6} ohm^{-1} cm^{-1}) from the conductivity of the solution. With solutions of Teepol and Petrowet, which are mixtures of several substances of varying equivalent weights, the equivalent conductivity based on an average equivalent weight has been used. The presence of inorganic salts and other compounds added to enhance the commercial value of these agents renders the absolute value of these "equivalent conductivities" doubtful.

RESULTS

The effect of various concentrations of the surface active agents on the rate of absorption of carbon dioxide by water flowing over the sphere was determined. Flow rates between 1 and 7·5 cc/sec of water were investigated and concentrations up to a maximum of 5% by volume. As shown by Figs. 1-4, the results for the commercial products were similar to one another in that, at a given liquid rate, the absorption fell sharply with small concentrations to a minimum, and eventually at much larger concentrations returned nearly to the theoretical rate. The theoretical rate was calculated as

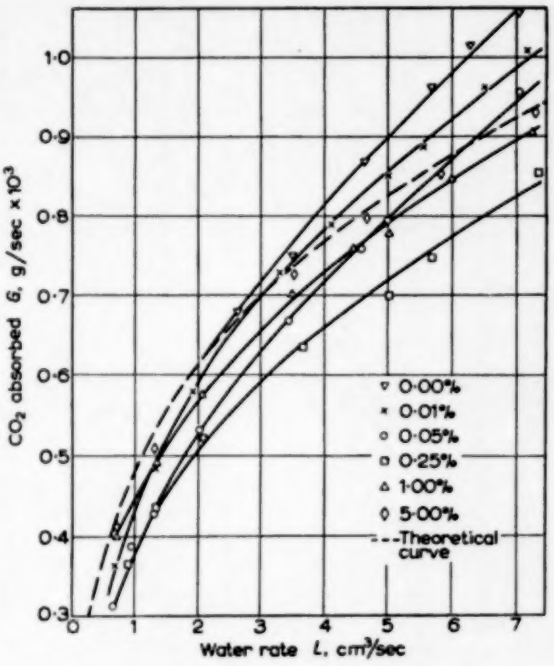

FIG. 1. Absorption rates with Teepol solutions.

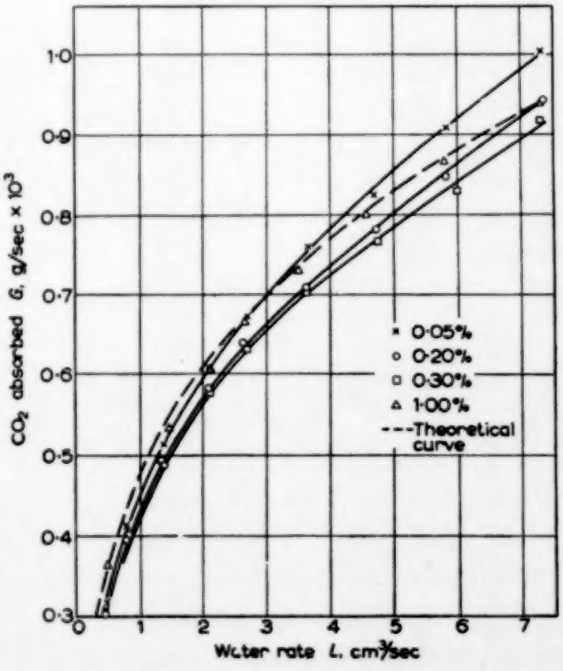

FIG. 2. Absorption rates with Petrowet solutions.

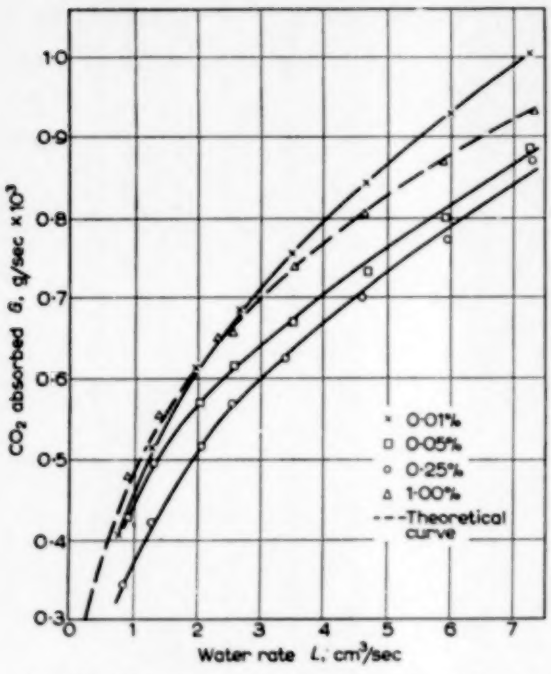

FIG. 3. Absorption rates with Lissapol solutions.

in reference [11]. With very low concentrations, and at liquid flow rates greater than 3 cc/sec, the absorption rates were greater than the theoretical due to rippling in the liquid film. The rippling was eliminated when the wetting agent exceeded a certain concentration, this being less than the concentration to give the minimum absorption rate.

Fig. 5 gives results for the pure sodium dodecyl sulphate. A solution containing 0·1 wt.% was used over the whole range of liquid flow rates, and at a flow rate of about 2 cc/sec, concentrations of 0·03, 0·2 and 0·3 wt.% were investigated. The results, which are compared with the theoretical absorption rate, show that pure sodium dodecyl sulphate has a negligible effect on the absorption.

Fig. 6 shows the variation of the absorption rate, with concentration, for a solution of pure sodium dodecyl sulphate plus 2% dodecanol (based on sulphate), at a liquid flow rate of 2 cc/sec.

Figs. 7 and 8 show the variation of the surface tension and equivalent conductivity with volume

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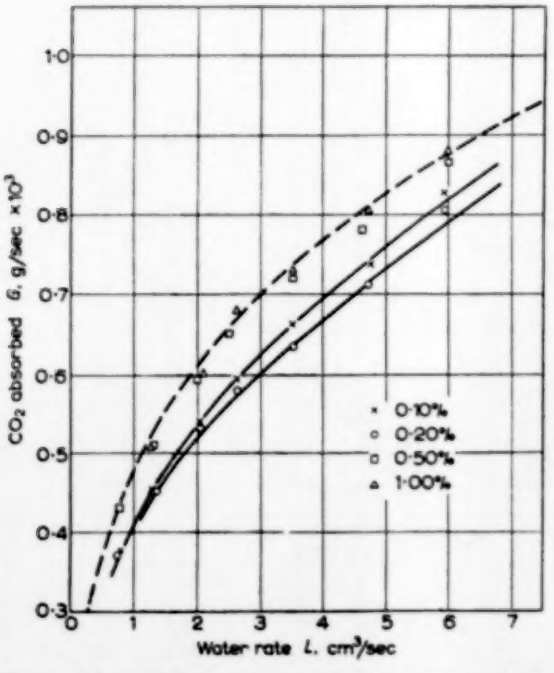

FIG. 4. Absorption rates with commercial sodium dodecyl sulphate solutions.

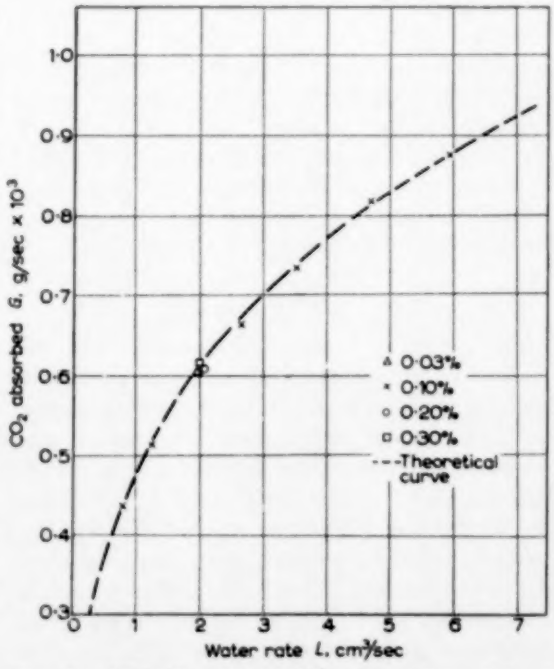

FIG. 5. Absorption rates with pure sodium dodecyl sulphate solutions.

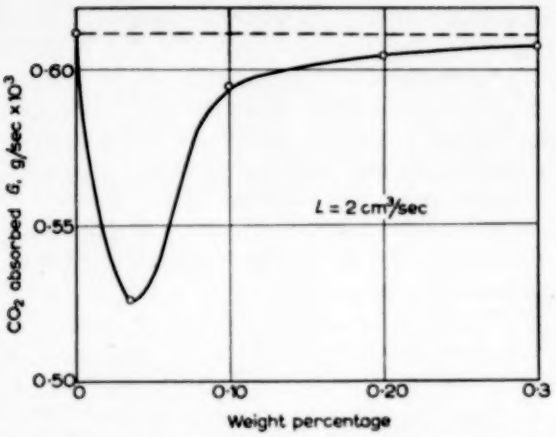

FIG. 6. Variation of absorption rate with concentration of pure sodium dodecyl sulphate + 2% dodecanol solutions. The horizontal dotted line represents the theoretical rate.

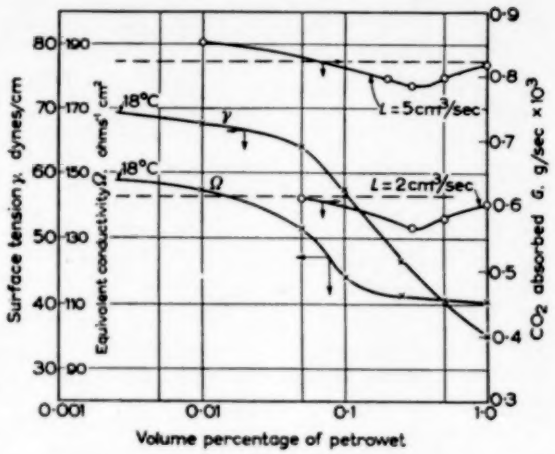

FIG. 8. Variation of absorption rate, surface tension and equivalent conductivity with concentration of Petrowet. The horizontal dotted lines represent the theoretical absorption rate.

concentration of Teepol and Petrowet R, together with the variation of the rate of gas absorption at liquid flow rates of 2 and 5 cc/sec. Fig. 9, for Lissapol N, is similar except that, being non-ionic, no conductivity data are recorded. Fig. 10, for commercial sodium dodecyl sulphate, is also similar, except that it is based on a weight instead of a volume percentage. These figures show that there is a rough connexion between the change in gas absorption and the changes in surface tension and conductivity. At large concentrations the absorption rate returns very nearly to the theoretical value. The variation of surface tension and equivalent conductivity with concentration for the pure sodium dodecyl sulphate was in good agreement with the values in the literature [15, 16]. All the surface tension and conductivity experiments were carried out near room temperature and the exact temperatures are recorded on the individual curves.

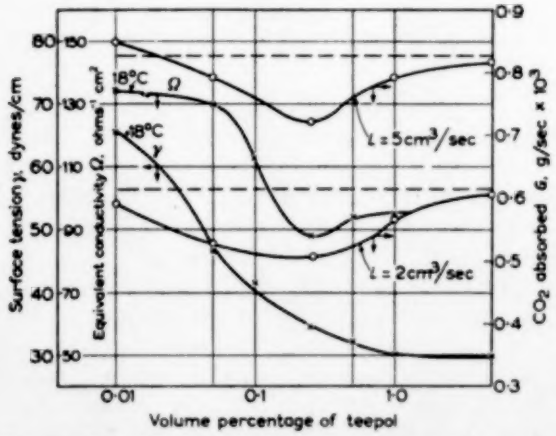

FIG. 7. Variation of absorption rate, surface tension and equivalent conductivity with concentration of Teepol. The horizontal dotted lines represent the theoretical absorption rate.

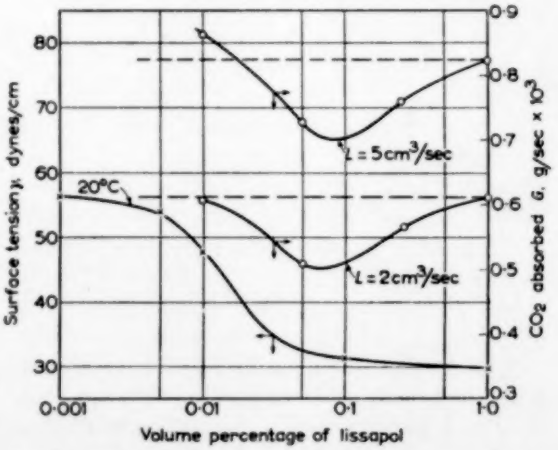

FIG. 9. Variation of absorption rate and surface tension with concentration of Lissapol. The horizontal dotted lines represent the theoretical absorption rate.

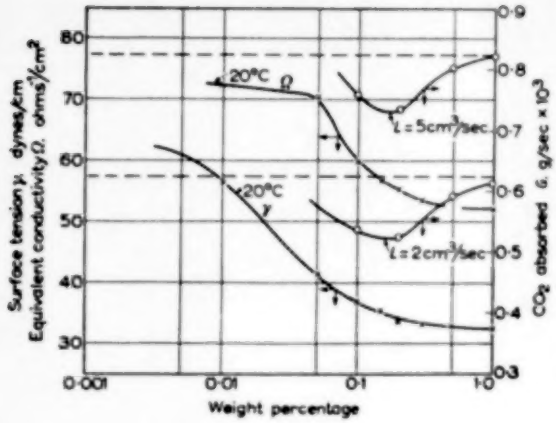

Fig. 10. Variation of absorption rate, surface tension and equivalent conductivity with concentration of sodium dodecyl sulphate. The horizontal dotted lines represent the theoretical absorption rate.

Discussion

The results shown in Figs. 7 to 10, using the commercial surface active agents, show that the region of depressed absorption rate is about the same as the region in which the surface tension and conductivity are changing. These changes are generally attributed to the formation of micelles of the surface active molecules or ions in the bulk of the solution. As the concentration is increased beyond this critical value, the resistance to gas absorption gradually decreases until at relatively high values it becomes negligible.

The suggested explanation of this effect is the same as that proposed by Miles and Shedlovsky [17] for a related effect. They found that small quantities of dodecanol added to solutions of very pure sodium dodecyl sulphate caused a minimum in the graph of surface tension versus concentration. This was attributed to the sparingly soluble dodecanol being preferentially adsorbed at the surface at low concentrations, but being desorbed back into the bulk of the solution after micelle formation had begun. The impurities in the commercial products might well cause a similar effect on the rate of gas absorption. Support for this idea was obtained from the results of experiments using very pure sodium dodecyl suphate, shown in Fig. 5. The The latter showed no resistance to gas absorption at any concentration up to 0·3 wt.%. However, as shown in Fig. 6, the addition of 2% of dodecanol (based on the sulphate) caused a high resistance to develop at concentrations less than 0·1 wt.%.

The reason for small quantities of impurities causing a resistance to gas absorption is very difficult to find. The possibility that the impurities might cause a high viscosity in the surface film, resulting either in a low diffusion coefficient or in a hydrodynamic effect, was investigated. Qualitative experiments were made on the movement of small particles on the surface of the solutions used, but only the impure sodium dodecyl sulphate and the pure material containing dodecanol showed a marked surface viscosity. In both cases, viscosity appeared to reach a maximum at a concentration corresponding to the maximum resistance to gas absorption and to decrease with increasing concentration. This effect has been measured quantitatively by Durham and Camp [18], who observed the same general effect for solutions of pure sodium dodecyl sulphate containing dodecanol. In another system, Blakey and Lawrence [19] found that small quantities of a soap produced abnormally high surface viscosities in an alcohol film, but that the effect decreased to zero with increasing concentrations above the critical. The other commercial products, however, showed no appreciable surface viscosity, and thus it seems that the rough correlation observed between the surface viscosity and resistance to mass transfer with impure sodium dodecyl sulphate is coincidental. However, more quantitative work on surface viscosities is required before definite conclusions may be drawn.

Another possible cause of the resistance is an interaction between the adsorbed film and the diffusing molecules. This interaction is not likely to be simply mechanical obstruction, owing to the extreme thinness of the surface film. The present experiments indicate that either the impurities alone or some combination of the impurities and the surface active agent constitute the resistance to mass transfer. That the latter

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is more likely is suggested by the results with pure sodium dodecyl sulphate, though the work of LINDLAND and TERJESEN [4] contradicts this idea. With increasing concentration of a pure surface-active agent, they found a reduction to a constant value in the overall extraction coefficient of iodine from water by drops of carbon tetrachloride. This was attributed to a surface resistance, but it could equally be interpreted as a hydrodynamic effect in which the internal circulation of the drop is suppressed by the surface active agent. This idea is supported by the sharp reduction of droplet velocities with small additions of the agent. GARNER and HALE [1], using Teepol, measured the overall coefficient for transfer from drops and found that the coefficient decreased to a minimum and subsequently increased steadily with increasing concentration of the agent. GARNER and SKELLAND [2], using more specific agents, found a similar effect, and the rise in the coefficient after the minimum was attributed to increasing deformation and oscillation of the drops. However, in the light of the present results, it seems probable that the rise is due to desorption from the interface of the impurities in the surface-active agents used. Thus the evidence on whether the impurities alone or some combination of the impurities and the agent produce the barrier to mass transfer is not conclusive, but the present work suggests it is the latter effect.

The data obtained by TERNOVSKAYA and BELOPOLSKII [6] on absorption in a wetted-wall column is more readily explicable. The initial increase in HTU on the addition of all three agents is almost certainly due to the elimination of rippling in the liquid film. The subsequent decrease in HTU observed with two of the agents is probably due to the desorption from the surface of impurities. EMMERT and PIGFORD's data [10] on a wetted-wall column is similar. Their results showed a surface resistance close to the value determined in the present work for the same agent. Their suggestion that the decrease in HTU after the maximum was due to the reappearance of rippling in the liquid film was qualitatively investigated, using a number of agents in a long wetted-wall column. In no case was it possible to detect any reappearance of ripples even at concentrations up to 5 vol.%.

SHERWOOD and HOLLOWAY [20] found that surface active agents had a similar effect on the rate of desorption of carbon dioxide in a packed tower. The explanation given for the data on wetted-wall columns is directly applicable, but uncertainty about the effect of the agent on the degree of wetting of the packing renders this further evidence less definite.

CONCLUSIONS

1. Impurities in commercial surface-active agents can cause a reduction up to 25% in the rate of gas absorption. This effect reaches a maximum near the critical concentration for micelle formation and, with increasing concentration, finally decreases to negligible proportions. The magnitude of the effect is specific to the material used.

2. Solutions of very pure sodium dodecyl sulphate show no resistance to gas absorption, but the addition of dodecanol causes a resistance to absorption.

3. The use of commercial surface-active agents to eliminate rippling may introduce a resistance to mass transfer. However, with very pure materials or with a sufficient concentration of commercial material, this resistance is very small.

4. The modified wetted-wall column used in the present work is very suitable for investigating the effect of surface-active agents on mass transfer, because the hydrodynamic conditions are well defined at the surface and it is possible to get good agreement between theory and experiment without adding any agent at all. However, relatively large quantities of material are required.

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Critical and terminal velocities in fluidization

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Abstract—Critical fluidization and terminal velocities of spherical and nonspherical particles were determined in nitrogen. The ratios of these velocities, or of their particle Reynolds numbers, are shown to be function of the dimensionless group

$$\frac{\mu^2}{g\,(\rho_s - \rho_0)\,\rho_0\,d^3}.$$

The ractical implications of the results are discussed.

Résumé—Les auteurs ont déterminé dans l'azote les vitesses critiques de fluidisation et les vitesses limites pour des particules sphériques ou non sphériques.

Les rapports de ces vitesses ou de leur nombre de REYNOLDS correspondant à la particule apparaissaient être une fonction du groupe sans dimension ci-dessus.

Examen des conséquences pratiques de ces résultats.

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1. INTRODUCTION

THE application of the technique of fluidization in the chemical industry is growing rapidly and is far outstripping the fundamental knowledge of the physical processes involved.

One aspect which has received much attention is that of the critical velocity at which fluidization starts and outstanding in this respect are the pioneering papers by LEVA and collaborators [1], WILHELM and KWAUK [2] and by VAN HEERDEN [3]. Less attention has been given, as far as fluidization is concerned, to the velocity at which particles are removed overhead from the bed, though this aspect has been studied in connection with such subjects as transport of solids. The work carried out in relation to fluidization has recently been reviewed [4] and terminal velocities in the fluidization of particles with water have received some attention by WILHELM and KWAUK [2]. VAN HEERDEN *et al* [5], from their work on heat transfer in fluid beds, obtained approximate ratios of terminal to critical mass velocities for fully turbulent and for streamlined conditions. LEVA [6] has studied the rate of removal of fine particles from a fluidized bed of fine and coarse components and has expressed his results in terms of a first-order rate equation. A useful summary unrelated to the subject of fluidization is also given by DALLAVALLE [7].

A general relation of initial fluidization velocity and terminal velocity would be of interest to the designer of fluidized solids reactors, where it is desired to avoid overhead loss of particles above any particular diameter from the reactor. The present study is the outcome of experiments in fluidized catalysis, where it was necessary to prevent overhead loss of particles without use of auxiliary equipment but it is believed that the relations derived below should also assist in the design of filters and cyclones in conventional fluidized reactors.

2. THEORETICAL

The free fall of small particles above about one micron diameter through a fluid is expressed by STOKES' Law,

$$Re_T = \frac{\rho_0\,(\rho_s - \rho_0)\,g d^3}{18\,\mu^2} \qquad (1)$$

For larger particles this equation is not valid. A relation for all sizes of particles has been derived by RUBEY [8] from theoretical considerations. The total force holding a particle in suspension at a constant height in a fluid current may be considered as the sum of viscous resistance and fluid impact

$$\frac{\pi d^3}{6}\,(\rho_s - \rho_0)\,g = 3\pi\,d\,\mu\,v_T + \frac{\pi d^2}{4}\,\rho_0\,v_T^2 \qquad (2)$$

Converting this equation by substitution of $\frac{Re_T \mu}{d \rho_0}$ for v_T and solving the quadratic equation we have

$$Re_T = -6 + \sqrt{36 + \frac{2}{3} g \frac{(\rho_s - \rho_0) \rho_0 d^3}{\mu^2}} \qquad (3)$$

A plot of Re_T *vs* d from the relation approaches the Stokes curve from equation (1) asymptotically as particle diameter decreases.

A measure of the interval in which particles are fluidized, but not removed from a vertical vessel is the ratio of Re_T/Re_0. It remains to decide on the equation for the critical particle Reynolds number (Re_0, at which fluidization starts) to be used. Both LEVA's [1] and VAN HEERDEN's [3] equations are based on the the CARMAN-KOZENY relation [9] but differ numerically. It is shown later that the results of the present work are fitted much more closely by the VAN HEERDEN equation [3] which for spherical particles reduces to

$$Re_0 = \frac{0{\cdot}00123 \times 0{\cdot}594 \, \rho_0 (\rho_s - \rho_0) g \, d_e^3}{\mu^2} \qquad (4)$$

if ρ_0 is not neglected.

Dividing equation (3) by equation (4) and replacing d by d_e (as defined by VAN HEERDEN) for the generalized case for particles of any shape

$$\frac{Re_T}{Re_0} = 8{\cdot}2122 \times 10^3 \frac{\mu^2}{\rho_0 (\rho_s - \rho_0) d_e^3 g} + \sqrt{6{\cdot}744 \times 10^7 \left(\frac{\mu^2}{\rho_0 (\rho_s - \rho_0) d_e^3 g}\right)^2 + 1{\cdot}2489 \times 10^6 \frac{\mu^2}{\rho_0 (\rho_s - \rho_0) d_e^3 g}} \qquad (5)$$

This ratio is obviously a function of the dimensionless group

$$\frac{\mu^2}{\rho_0 (\rho_s - \rho_0) d_e^3 g}$$

which we may call the fluidization number, *Fl*. In this form the equation is applicable to all fluids and spherical solids and in the case of gases or vapours where ρ_0 may be neglected in comparisen with ρ_s, the group may be reduced to $\frac{\mu^2}{\rho_0 \rho_s d_e^3 g}$. This dimensionless group, in its generalized form, is equivalent to $\frac{1}{2K_\Delta \rho}$ as used by WILHELM and KWAUK [2] to express generalized pressure drop-velocity relationships for all particles and fluids.

The accuracy of relation (5) was tested experimentally.

3. EXPERIMENTAL

Experiments were carried out in a 2-inch diameter glass tube with nitrogen at room temperature. For the largest particles a 3-inch tube was used to determine Re_0 and a 1-inch tube for Re_T.

Re_0 was measured by finding the velocity at which the pressure drop across the bed equalled the static pressure. The terminal velocity for spheres was determined by gradually increasing the nitrogen flow till particles began to be elutriated at the top of the tube. The particles were collected and the largest diameter of the particles carried over was determined microscopically.

With nonspherical particles nitrogen was passed through the bed at such a rate as to remove the finest material and the bed maintained for some time in this condition. When apparently no more particles were elutriated at this rate the nitrogen velocity was increased slightly and the particles now carried over were collected and d_e, the effective diameter, determined using VAN HEERDEN's technique [3].

The densities of the particles in mercury ρ_s, were determined in a modified density bottle at room temperature. Samples of the materials were sieved through

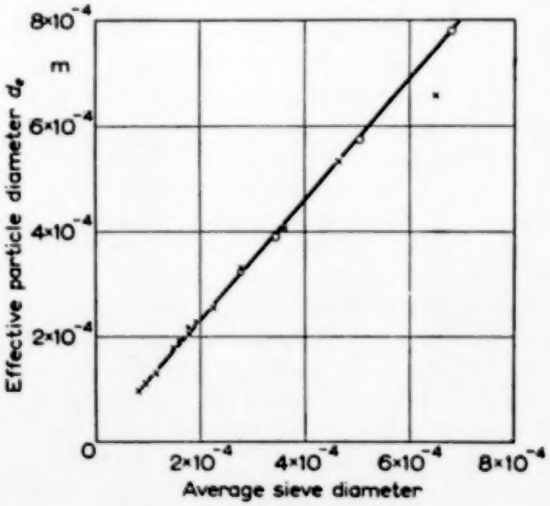

FIG. 1. ○ Authors results
× VAN HEERDEN results

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Table 1. *Fluidization in nitrogen at* 18°C $\rho_0 = 1{\cdot}18\ kg/m^3$ $\mu = 1{\cdot}73 \times 10^{-5}\ kg/m\ sec.$

Material	*Shape*	*Density* kg/m^3	*Average diameter* d_s $m \times 10^6$	*Effective diameter* d_e $m \times 10^6$	G_0 $kg/m^2\ sec$	Re_0
Glass "Ballotini"	Spherical	2990	108	108	0·0126	0·079
			165	165	0·0303	0·290
			221	221	0·055	0·705
			354	354	0·139	2·850
			750	750	0·417	18·10
			1990	1990	1·060	122
Microspherical catalyst	Mainly spherical	1870	225	225	0·038	0·494
			335	335	0·083	1·610
			480	480	0·168	4·660
Microspherical alumina	Mainly spherical	1170	55	55	0·0013	0·0041
			96	96	0·0040	0·0222
			225	225	0·022	0·286
Ground silica	Non-spherical	1255	225	257	0·031	0·460
			335	385	0·065	1·440
			480	550	0·135	4·300

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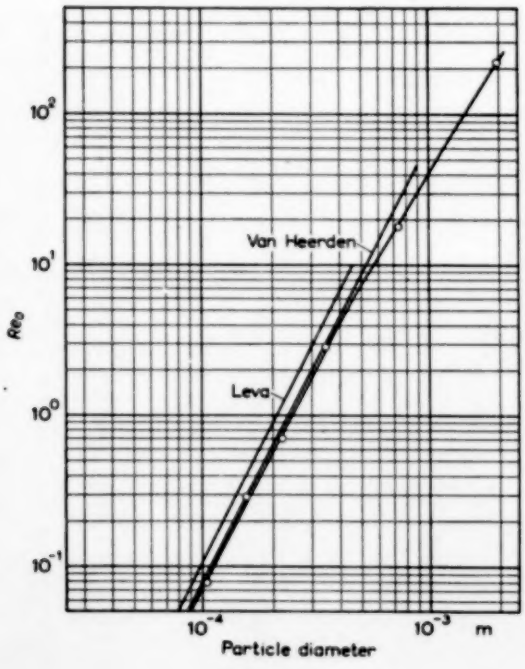

Fig. 2.

standard sieves selected so that the bulk had a spread of about 10% from the mean diameter. In the case of spherical particles the average diameter was determined by microscopic measurement of 50 to 100 particles.

The average effective diameter d_e of nonspherical particles could be obtained from the straight line relationship of d_e and d_s, the mean sieve diameter, which was found in a subsidiary experiment to exist for these particles (see Fig. 1).

4. Results

The properties of the solid particles used in the experiments are given in Table 1 together with the experimental results for the critical Reynolds number. In Fig. 2 the van Heerden and Leva equations are superimposed on a plot of the experimental results for glass spheres and it is clear that the former results in a much better fit. Above a diameter of $5{\cdot}5 \times 10^{-4}$ m, Re_0 is no longer a function of d^3 and van Heerden's equation is no longer obeyed.

The terminal velocities for the particles are listed in Table 2. As the terminal velocity was always that of the smallest particle in the particular size range the d_e values in Tables 1

Table 2. Terminal velocities in nitrogen at $18°C$ $\rho_0 = 1{\cdot}18\ kg/m^3$ $\mu = 1{\cdot}73 \times 10^{-5}\ kg/m\ sec.$

Material	*Shape*	*Effective diameter* d_e $m \times 10^6$	G_0 $Kg/m^2\ sec$	G_T $Kg/m^2\ sec$	Re_0	Re_T	$\frac{Re_T}{Re_0}$	$= \frac{Fl}{\mu^2 / g\rho_0(\rho_s - \rho_0)d^3}$
Glass "Ballotini"	Spherical	85	0·0076	0·467	0·0373	2·30	61·4	$14{\cdot}1 \times 10^{-3}$
		93	0·0091	0·546	0·0490	2·94	60·0	$10{\cdot}8 \times 10^{-3}$
		157	0·027	1·105	0·245	10·0	40·8	$2{\cdot}24 \times 10^{-3}$
		177	0·035	1·231	0·358	12·6	35·2	$1{\cdot}56 \times 10^{-3}$
		193	0·042	1·305	0·469	14·6	31·1	$1{\cdot}20 \times 10^{-3}$
		207	0·048	1·370	0·574	16·4	28·6	$9{\cdot}76 \times 10^{-4}$
		229	0·058	1·485	0·769	19·6	25·6	$7{\cdot}21 \times 10^{-4}$
		264	0·077	1·650	1·173	25·2	21·5	$4{\cdot}70 \times 10^{-4}$
		770	0·420	5·540	18·70	246	13·2	$1{\cdot}90 \times 10^{-5}$
		1990	1·060	12·130	122	1395	11·4	$1{\cdot}10 \times 10^{-6}$
Microspherical catalyst	Mainly spherical	195	0·0285	0·970	0·321	11·0	34·2	$1{\cdot}87 \times 10^{-3}$
		250	0·0460	1·190	0·664	17·1	25·8	$8{\cdot}9 \times 10^{-4}$
		285	0·0590	1·300	0·972	21·4	22·0	$6{\cdot}0 \times 10^{-4}$
		300	0·0660	1·310	1·142	22·6	19·8	$5{\cdot}1 \times 10^{-4}$
		364	0·0960	1·525	2·020	32·1	15·9	$2{\cdot}9 \times 10^{-4}$
		400	0·115	1·675	2·660	38·8	14·6	$2{\cdot}2 \times 10^{-4}$
Microspherical alumina	Mainly spherical	24	0·00025	0·0191	0·00035	0·0268	76·5	1·60
Ground silica	Non spherical	95	0·0040	0·229	0·0220	1·26	57·1	$2{\cdot}41 \times 10^{-2}$
		150	0·0101	0·463	0·0875	4·02	45·9	$6{\cdot}11 \times 10^{-3}$
		345	0·0540	0·880	1·077	17·6	16·3	$5{\cdot}0 \times 10^{-4}$
		440	0·0860	0·930	2·186	23·6	10·7	$2{\cdot}4 \times 10^{-4}$

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and 2 do not correspond. The values for Re_0 given in Table 2 were obtained from plots of Re_0 vs. d_e for each type of material. The ratio $\frac{Re_T}{Re_0}$ found from the interpolated values of R_0 and the experimental values of Re_T is also given in Table 2. The experimental values of Re_T for glass spheres are plotted in Fig. 3 with RUBEY's equation.

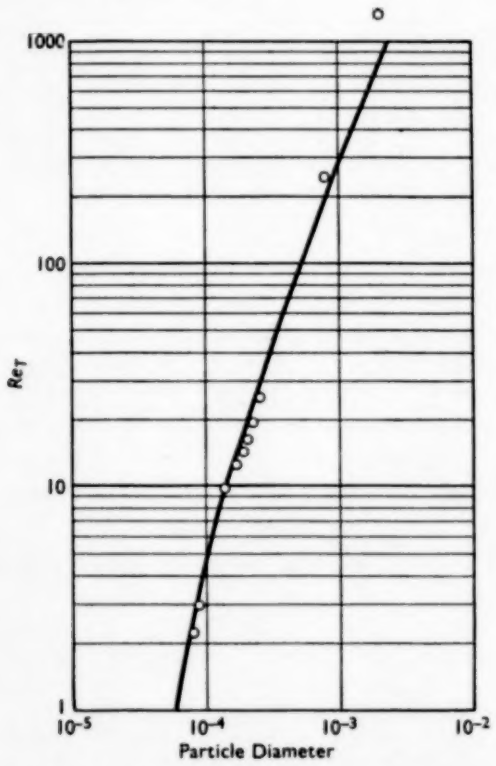

FIG. 3. ○ Experimental results (Glass spheres)
Theoretical curve (Rubey)

5. DISCUSSION

The equation for the terminal velocity used in this study (eq. 3) represents the experimental results reasonably well. The scatter about the line is probably largely due to experimental error, but some real deviation from RUBEY's equation seems to exist for the larger particles. For the present purposes, however, RUBEY's equation is a good representation of the results.

The experimental critical Reynolds numbers with values below 10 are all slightly lower than the values calculated from the VAN HEERDEN equation, but a sufficiently good fit for the VAN HEERDEN equation is to be accepted.

For the larger particles (see Fig. 2), however, the equation is obviously not valid. According to VAN HEERDEN the equation is only valid for the region of viscous flow, i.e. up to Reynolds numbers of about 10. The present results indicate that the limiting value is correct.

Whereas in the region of viscous flow Re_0 is proportional to d_e^3 the proportionality apparently changes gradually to $d_e^{1.5}$ as the particle size increases. This change in proportionality occurs also in the terminal Reynolds number (dependence of d_e^3 here also ceases around $Re_T \approx 10$) and is formalised in RUBEY's equation. A modification of the VAN HEERDEN equation along similar lines should provide a relation valid for all conditions; however, such an expression would prove very unwieldy and would, in any case, be of only limited usefulness.

The ratios $\frac{Re_T}{Re_0}$ from the experimental results obtained in this study are plotted in Fig. 4 together with the line calculated from equation (5). Also included in this figure are values obtained from the data of WILHELM and KWAUK [2] for fluidization of particles in water. The fit for the spherical particles is very good. The ratio $\frac{Re_T}{Re_0}$ for nonspherical particles is somewhat smaller than calculated but even here the relation is obeyed quite well. In the derivation of VAN HEERDEN's equation it is shown that the shape factor of irregular particles approaches 1 if effective particle diameter is used instead of average particle diameter and it has been tacitly assumed above that the same holds for RUBEY's equation. A comparison of the experimental and calculated values of Re_T for nonspherical particles, shows this assumption to be incorrect, whereas it is found to be reasonably accurate in the case of Re_0. Therefore, the experimental ratio probably deviates from the calculated one because of the absence of a shape factor in RUBEY's equation. Despite these

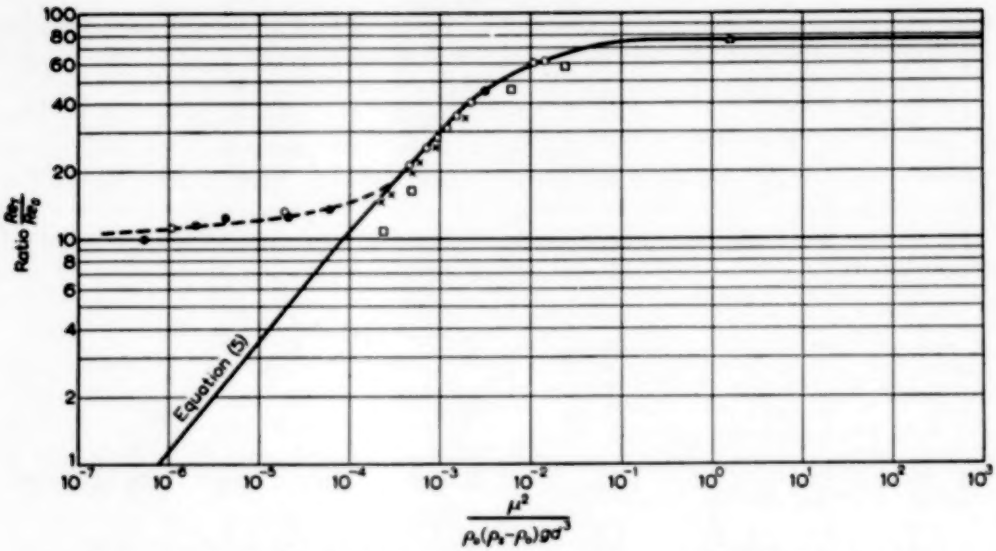

FIG. 4. ○ Glass 'Ballotini' △ Microspherical alumina × Microspherical catalyst
□ Ground silica ● From data of WILHELM and KWAUK

deviations the fit of the experimental points to the calculated line is sufficiently good to give confidence in the validity of equation (5) for fluidization numbers above $\approx 3 \times 10^{-4}$. Whereas RUBEY's equation is obeyed for lower fluidization numbers, VAN HEERDEN's equation is not, as has been pointed out above, and the experimental points suggest that the true curve should follow the line indicated by dashes which approaches a constant ratio $\frac{Re_T}{Re_0}$ for very small fluidization numbers, i.e. very large particles. If equation (5) were correct in that region a point would be reached where $\frac{Re_T}{Re_0}$ would become less than 1, i.e. particles would be elutriated without fluidization having set in. The values of WILHELM and KWAUK also lie close to the modified curve and demonstrate the validity of the curve for fluidization both in gas and in liquid.

It is interesting to consider the physical significance of the curve (Fig. 5). Its plot shows five distinct branches. The first branch for very large fluidization numbers indicates virtually constant ratio, due to the dependence of both Re_0 and Re_T on the cube of particle diameter. This is the region of STOKES's law and the ratio

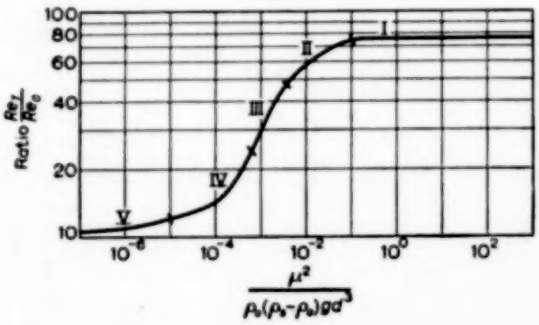

FIG. 5.

of $\frac{Re_T}{Re_0} \approx 76$ can also be obtained if STOKES's law (equation 1) is divided by equation 4. This branch will be limited by the validity of STOKES's law. (STOKES's law is not obeyed by particles of less than 1 micron diameter). The ratio of 76 represents the greatest possible flexibility between critical and terminal Reynolds numbers (and therefore mass velocities) attainable in a fluidized reactor without overhead loss of particles.

Section 2 of the curve is the region of change of terminal velocity from viscous to turbulent with a gradual change of slope, while Re_0 remains proportional to d_s^3.

Eventually the terminal velocity becomes fully turbulent and Re_T will then be proportional to $d_e^{1.5}$. If the limitations on the VAN HEERDEN equation previously referred to did not exist, this would result in the straight line portion of slope 1·5 starting around section 3. In actual fact section 3 of the curve is very short and may be only an inflection point; the slope then changes again in section 4 as the critical fluidization velocity changes from viscous to turbulent

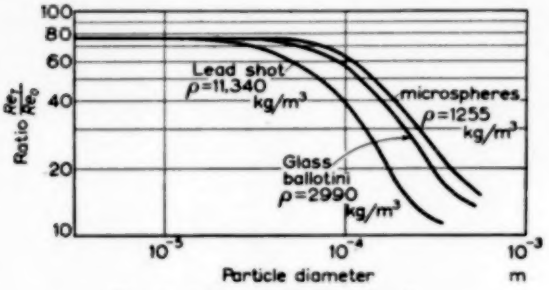

FIG. 6. Effect of particle density.
Fluidizing gas-nitrogen. Temperature 20°C.

with a change of the proportionality of Re_0 from d_e^3 to $d_e^{1.5}$. When the critical velocity is fully turbulent both Re_0 and Re_T are proportional to $d_e^{1.5}$ and their ratio consequently has a constant value of about 10, as in part 5 of the curve.

It is of interest to note that VAN HEERDEN *et al* [5] proposed values of 70 for the streamlined region (corresponding to Section 1 of the curve) and 8·5 for the fully turbulent region (i.e. Section 5); these are in good agreement with the present results.

The relationship of $\frac{Re_T}{Re_0}$ may have practical implications in the design of a fluidized catalyst reaction vessel, where elutriation of particles is to be avoided and it may also be useful in the des gn of filtration equipment in fluid catalyst reactors with particles of a wide range of diameters. Its practical implications may be discussed briefly. Flexibility, that is the number of times the critical fluidization velocity may be exceeded, varies from 76 for the smallest to about 10 for the largest particles. The actual diameters, for which these values are attained, depend on solid density and the density and viscosity of the fluidizing medium. To reach the value of 76, smaller particles are required for heavier catalysts. (See Fig. 6). Fluid density has a similar and fluid viscosity an opposite effect, hence increasing temperature with gas or vapour as the fluidizing medium causes the fluidization number to increase rapidly for any given particle diameter, i.e. greater operating flexibility is possible at higher

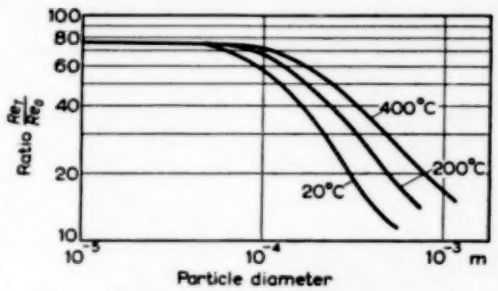

FIG. 7. Effect of fluidizing gas temperature.
Particles – Glass 'Ballotini.' Gas-Nitrogen.

temperatures (see Figure 7). Flexibility is also increased with spherical catalyst compared with ground catalyst of the same effective diameter.

Acknowledgement—The authors wish to thank Mr. A. SCHOFIELD for his help in the experimental work and the Council of the Coal Tar Research Association for permission to publish this paper.

NOTATION

d = diameter of particle m
d_e = effective diameter m
d_s = arithmetical mean diameter (of narrow diameter range) m
$Fl = \frac{\mu^2}{\rho_0 (\rho_s - \rho_0) d_e^3 g}$ = fluidization number
g = acceleration due to gravity 9·8 m/sec²
G_0 = critical fluidization velocity kg/m² sec
G_T = terminal mass velocity kg/m² sec
$K_{\Delta\rho} = \frac{1}{2Fl}$
$Re_0 = \frac{G_0 d_e}{\mu} = \frac{G_0 d}{\mu}$ for spherical particles
$Re_T = \frac{G_T d_e}{\mu} = \frac{G_T d}{\mu}$ for spherical particles
v_T = linear terminal velocity m/sec
μ = dynamic viscosity kg/m sec
ρ_0 = density of fluidizing medium kg/m³
ρ_s = density of solid kg/m³

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Circulation in liquid drops

(A heat-transfer study)

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Abstract—The process of material and heat transfer to and from liquid drops moving through another continuous fluid has been examined. Continuous phase heat-transfer coefficients have been measured for the system mercury-aqueous glycerol solutions in which the mercury constituted the disperse phase. These data are in good agreement with those previously reported for solid spheres up to a Reynolds number of about 200, at which point drop oscillation commences.

The resistance to heat transfer of the disperse phase, expressed as an effective thermal diffusivity, has also been measured, for the system bromobenzene-aqueous glycerol solutions. These results were found to be in general agreement with much reported work and with the mathematical model of KRONIG and BRINK which applies to liquid drops undergoing internal circulation.

Some observations concerning the rigid, circulating, and oscillating behaviour of drops are made. The conclusion is reached on both experimental and theoretical grounds that circulation within a liquid drop results in an effective mass or thermal diffusivity of 2·25 times the molecular value. This result applies for the whole régime of circulation which exists between rigid sphere and oscillating behaviour. The onset of drop oscillation results in a considerable increase in this factor. Some effective diffusivities are reported for the oscillating régime which has not however been sufficiently studied to enable firm conclusions to be drawn.

Drag coefficients for falling liquid drops in the above-mentioned systems are also reported and reveal the limitations of recent correlations in this field.

Résumé—Les auteurs examinent le mécanisme du transfert de matière et de chaleur vers ou à partir de gouttes liquides se déplaçant dans un autre fluide continu. Les coefficients de transfert thermique dans la phase continue ont été mesurés pour le système mercure-solution aqueuse de glycérine dans lequel le mercure constitue la phase dispersée. Les valeurs obtenues concordent avec celles déjà obtenues pour des sphères solides jusqu'à un nombre de REYNOLDS d'environ 200, valeur à partir de laquelle commence l'oscillation de la goutte.

Exprimée sous forme d'une diffusivité thermique effective, la résistance à l'échange thermique de la phase dispersée a été également mesurée pour le système bromobenzène-solutions aqueuses de glycérine. Les résultats sont en concordance satisfaisante avec la majorité des travaux décrits et avec le modèle mathématique de KRONIG et BRINK qui s'applique à des gouttes liquides présentant une circulation interne.

Les auteurs ont fait quelques observations relatives au comportement de gouttes, rigides, en circulation ou en oscillation. A partir de résultats expérimentaux et théoriques, ils arrivent à la conclusion que la circulation à l'intérieur d'une goutte liquide entraîne une diffusivité thermique ou massique d'environ 2,25 fois la diffusivité moléculaire. Ce résultat s'applique à la totalité du régime de circulation s'étendant de la sphère rigide à la sphère oscillante. L'amorçage d'oscillation de la goutte entraîne un accroissement considérable de ce facteur. Les auteurs donnent quelques valeurs de diffusivité effective pour un régime oscillant qui n'a pas encore été suffisamment étudié pour permettre des conclusions définitives.

Les coefficients de traînée pour des gouttes liquides tombant dans les deux systèmes mentionnés ci-dessus indiquent les limitations des corrélations récentes dans ce domaine.

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INTRODUCTION

A RIGOROUS analysis leading to the prediction of the performance of spray columns in any of their varied applications requires a knowledge of the following quantities :—

1. Drop size.
2. Drop velocity.
3. Continuous phase heat or mass transfer coefficient.
4. Effective thermal or mass diffusivity within the drop.

Drop size data have been correlated by HEYWORTH and TREYBAL [1] in terms of nozzle diameter and the physical and flow characteristics of the system. Drop velocities have been correlated most recently by HU and KINTNER [2].

Continuous phase heat and mass transfer coefficients for systems involving solid spheres have been reported and are summarized by MCADAMS [3] and SHERWOOD and PIGFORD [4].

If the drop is assumed to behave as a rigid sphere in which transfer rates are solely determined by the value of the molecular diffusivity, it becomes possible to design a spray column from the foregoing correlations using the Grober chart [5]. This chart presents in convenient form the solution to the mathematical problem of summing the continuous and disperse phase resistances. A restriction imposed by the use of the Grober chart is that the temperature or concentration obtaining in the continuous phase be constant. For most practical cases, this condition would not be realized. If, however, the equilibrium and operating lines are linear, the solution of AMUNDSEN [6] may be used. The latter method is prohibitively laborious and a convenient general solution perhaps employing stepwise methods would be most desirable. However, even if such a method were developed, a serious objection remaining would be caused by the observation of GARNER [7] and others, that the liquid drop is generally in a state of internal motion. The use of the molecular diffusivity instead of some enhanced effective value, would therefore be expected to lead to serious overdesign.

The purpose of the present paper was that of evaluating the continuous phase-resistance and the effective diffusivity obtaining during the unhindered fall of drops.

In the circulating régime, it was demonstrated that the continuous-phase transfer resistance follows closely that reported for solid spheres, while the effective diffusivity within the drop is a constant multiple of the molecular diffusivity.

General Principles

It was decided, at the outset of this work, to study the process of heat rather than mass transfer within drops as previous workers have clearly demonstrated the difficulties in studying the process of mass transfer where trace contaminants, by their accumulation at the interface, lead to inconsistent results. Every precaution was however taken to ensure scrupulous cleanliness of the fluids and equipment.

Drop sizes and terminal velocities were measured directly as was the continuous phase-heat-transfer coefficient. The continuous phase-heat-transfer coefficient was evaluated in a series of experiments in which mercury drops were allowed to fall through hotter or colder aqueous solutions of glycerol. The resistance to heat transfer of the mercury drops was calculated to be a negligible fraction of the total resistance in these experiments in which a wide range of Reynolds and Prandtl numbers was obtained by variation of the amount of glycerol in the solution. It was found that the heat transfer during drop formation could be practically eliminated by allowing the drops to form in air at one drop diameter above the continuous phase.

In a further series of otherwise identical experiments, bromobenzene was used as the disperse phase. In this case the resistance to heat transfer of the drops was large. The resistance to heat transfer of the disperse phase was deduced from the measured overall resistance by making proper allowance for that of the continuous phase, as evaluated in the experiments with mercury drops. As it did not prove feasible to form the drops above the continuous phase, a correction had to be applied to allow for heat transfer during drop formation.

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Drag Coefficients

Drag coefficients were determined for mercury and bromobenzene drops falling through aqueous glycerol solutions.

Drop velocities were then deduced in the usual manner from a plot of $f \cdot (Re)^2$ against Re where for spherical drops $f \cdot (Re)^2 = \dfrac{4\, gd^3\, (\rho_d - \rho_c)\, \rho_c}{3\, \mu_c^2}$.

In the experiments with mercury drops, a number of nozzles were calibrated so that the drop size obtained in the heat-transfer experiments was known. When bromobenzene was used as the disperse phase, it was found more reliable to measure the drop size during the course of the heat-transfer experiments.

The Continuous-Phase Resistance

It may be easily shown from a heat balance, integrated for the case of a constant continuous phase-temperature, that the continuous-phase heat-transfer coefficient may be deduced from experimental data by means of the relationship :

$$h_c = \frac{Cp_d\, \rho_d \cdot d}{6} \cdot \frac{v_d - v_c}{L} \cdot \ln \frac{Ti - To}{To - Tc} \qquad (1)$$

Further, h_c may be correlated in the usual way with the physical and flow properties of the system from the functional relationship :

$$Nu = f(Re, Pr) \qquad (2)$$

Disperse-Phase Resistance

Under conditions of constant continuous-phase temperature and negligible continuous-phase resistance, the equation for diffusion in a rigid sphere, due to NEWMAN [8] is :

$$E = \frac{Ti - To}{Ti - Tc} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\frac{\alpha\, \pi^2\, n^2\, t}{r^2}}}{n^2} \qquad (3)$$

VERMEULEN [9] showed that this result could be accurately represented by the empirical equation:

$$E = \left(1 - e^{-\frac{\alpha\, \pi^2\, t}{r^2}}\right)^{\frac{1}{2}} \qquad (4)$$

KRONIG and BRINK [10] included the effects of internal circulation on diffusion and for $Re < 1$ and at zero-interfacial tension derived :

$$E = 1 - \frac{3}{8} \sum_{n=1}^{\infty} A_n\, e^{-\frac{\mu_n \cdot 16\, \alpha\, t}{r^2}} \qquad (5)$$

where the eigenvalues A_n and μ_n have been tabulated [11].

DANCKWERTS [12] has pointed out that equation (5) may not be as strictly limited as the above restrictions suggest.

Equation (5), which applies under conditions of constant continuous phase temperature and negligible continuous phase resistance was found in the present work to be well represented by the empirical equation :

$$E = \left(1 - e^{-2{\cdot}25\, \frac{\alpha\, \pi^2\, t}{r^2}}\right)^{\frac{1}{2}} \qquad (6)$$

This fact is demonstrated in Fig. 1 in which equations (3) and (4) and equations (5) and (6) are compared.

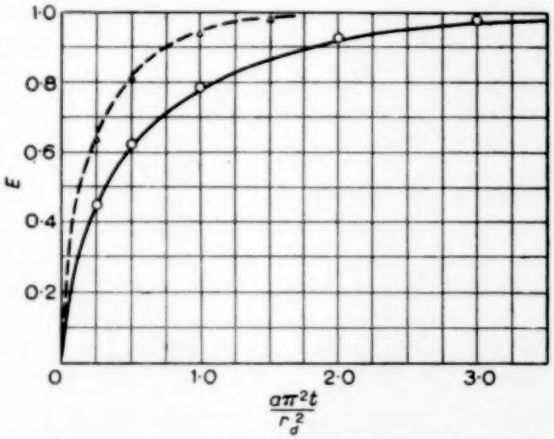


FIG. 1. Equations for diffusion into stagnant and circulating drops.

E vs. $\frac{\alpha\, \pi^2\, t}{r_d^2}$ PLOT

——— equation (3); — — — equation (5); ○ equation (4); △ equation (6).

If equations (4) and (6) are compared it may be readily seen that internal circulation of the type envisaged by KRONIG and BRINK may be represented by a constant effective diffusivity equal to 2·25 times the molecular value.

Finite Resistance in Both Phases

GROBER [5] has solved the equation for diffusion into a sphere in the case where the continuous

phase-resistance is finite. These results have been put into a convenient form and plotted in Fig. 2.

The restriction of constant continuous phase-conditions still applies to the proper use of Fig. 2.

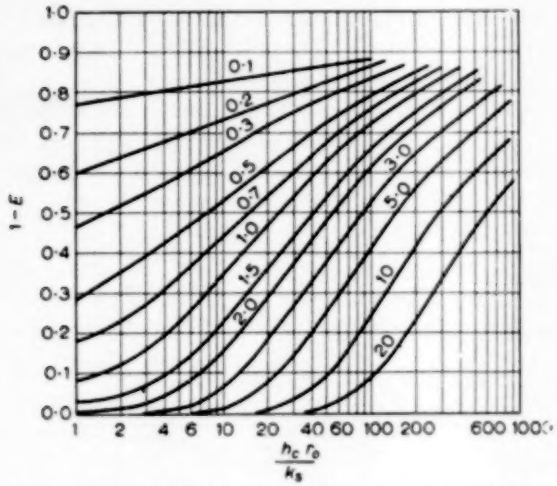
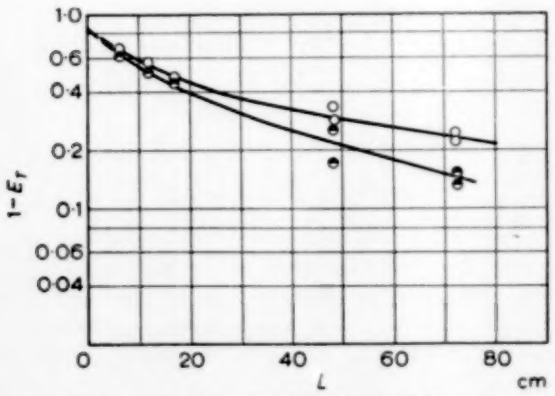


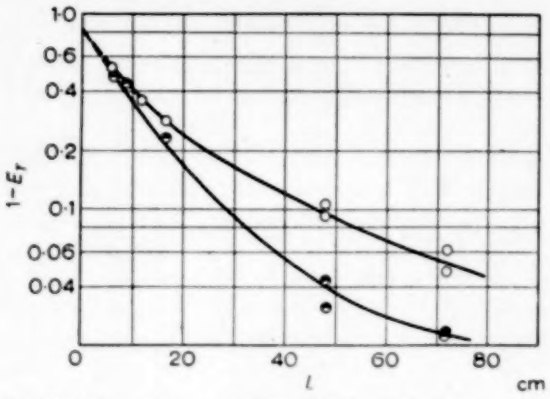
FIG. 2. Equations for diffusion into spheres with finite continuous-phase resistance.

Transfer during Drop Formation

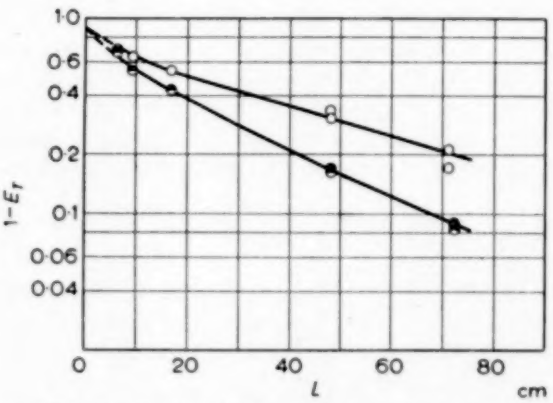
The extent of heat transfer during drop formation may be determined approximately by plotting experimental values of $-\ln(1 - E_T)$ against the column length for experiments in which the latter is varied, and extrapolating the curves to zero column length.



(a) Plot of $-\log(1 - E_T)$ vs. L for bromobenzene. Drops falling in 56·5% glycerol solution.
$E_F = 0{\cdot}15$
● Nozzle No. SS-1. ○ Nozzle No. 22-S.



(b) Plot of $-\log(1 - E_T)$ vs. L for bromobenzene. Drops falling in 28·7% glycerol solution.
$E_F = 0{\cdot}16$
● Nozzle No. SS-1. ○ Nozzle No. SS-2.



(c) Plot of $-\log(1 - E_T)$ vs. L for bromobenzene. Drops falling in 74·3% glycerol solution.
$E_F = 0{\cdot}12$
● Nozzle No. SS-1. ○ Nozzle No. SS-2.

FIG. 3. Heat transfer during bromobenzene drop formation as determined by extrapolation procedure.

This procedure is not rigorous since a linear driving potential is assumed but was adopted in this work in default of a better method.

The fractional approach to equilibrium during drop fall may be found from :

$$E_M = \frac{E_T - E_F}{1 - E_F} \qquad (7)$$

As previously stated, it was found possible to form mercury drops just above the continuous phase-surface and to thereby reduce the experimental value of E_F to zero.

In the case of bromobenzene, the above procedure led to distortion as the drop moved through the continuous phase-surface and drops had therefore to be formed below the surface when finite values of E_F lying between 12 and 16% were recorded (see Fig. 3).

Experimental Details

Physical Properties of Liquids

Reagent ACS grade 97·8% glycerol by weight was made up into solutions of various concentrations as determined by refractive index measurements. The specific heats of the solutions were obtained from Perry [13], the densities from the international critical tables [14], the thermal conductivities from the data of Bates [15] and the viscosities from the data of Sheeley [16].

Mercury was taken from the supplier and redistilled. Physical properties were obtained from the *Handbook of Chemistry and Physics* [17].

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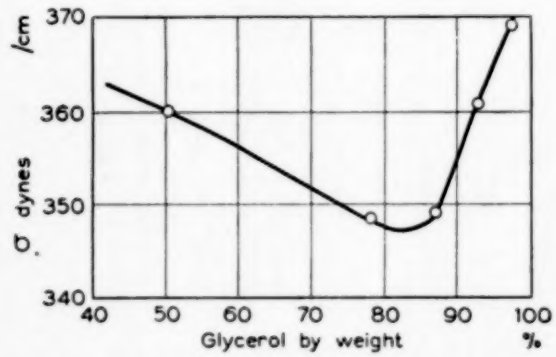
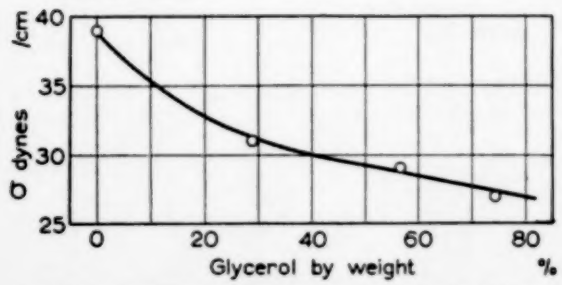


(a) Interfacial tension between mercury and glycerol-water solutions.



(b) Interfacial tension between bromobenzene and glycerol water solutions.

Fig. 4. Interfacial tension between mercury and glycerol solutions and between bromobenzene and glycerol solutions.

Interfacial tensions between mercury and glycerol water solutions were determined using the drop-weight method of Harkins and Humphrey [18] results being shown in Fig. 4.

Bromobenzene was obtained from BDH (boiling range 154°C to 158°C). The refractive index as measured was 1·5599 compared with the value of 1·55977 quoted in the International Critical Tables [14].

Interfacial tensions of bromobenzene in aqueous glycerol solutions were measured by the pendant drop-method [19]. The solubility of bromobenzene in glycerol solutions was found to be too small to be detected.

Nozzles

Five glass nozzles were prepared from capillary tubing and precision ground to a flat face, the tip nozzle diameter being measured with a toolmaker's microscope. Two sharp-edged stainless-steel nozzles were also used. The internal diameter of the nozzles ranged from 0·0328 cm to 0·4320 cm.

Drop Sizes

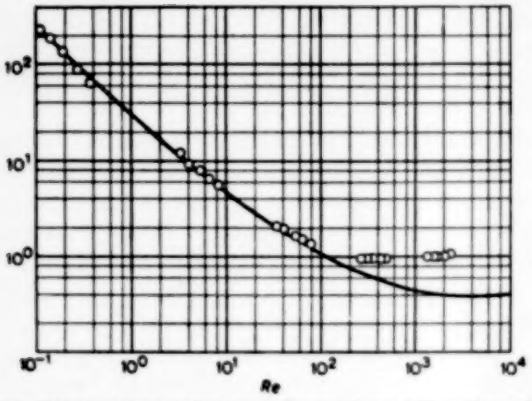
Drop sizes were measured by observing the volume of disperse phase formed when a measured number of drops had coalesced. As drop rates varied from 1 to 5 per second, a photocell and electronic counter were used to count the number of drops. Mercury drops were obtained varying in size from about 0·2 to 0·3 cm diameter. Bromobenzene drops lay in the size range 0·386 to 0·540 cm diameter.

Drop Velocities

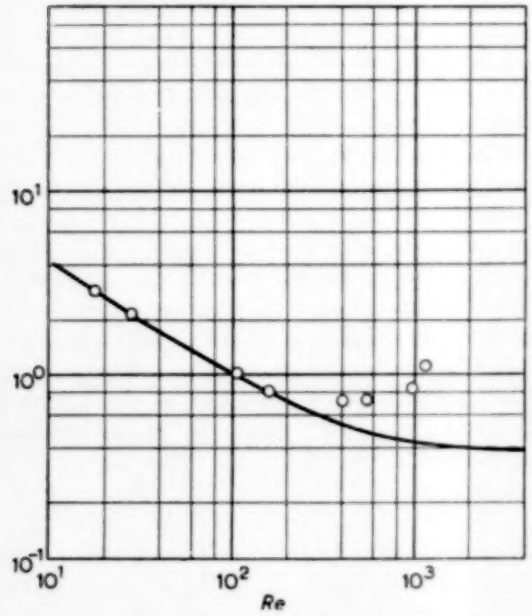
Drop velocities were determined by photographic means. By the use of a "stroboloom" in a darkened room, several photographic exposures at regular time intervals of a drop falling through the continuous phase were obtained.

The frame of the photograph also included an accurate linear scale. Results, plotted in terms of drag coefficients are shown in Fig. 5.

High-speed photographs were taken with a "Fastax" camera and showed that terminal velocities were attained at a point very close to the nozzle. It was also seen that mercury drops, formed one drop diameter above the continuous



(a) Friction factor plot for mercury drops falling through glycerol-water solutions.
○ exp. data. ——— solid spheres line.

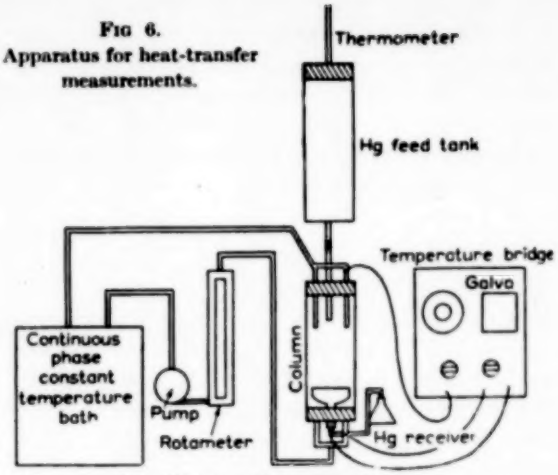


(b) Friction factor plot for bromobenzene drops falling through glycerol-water solutions.
○ exp. data. ——— solid spheres line.

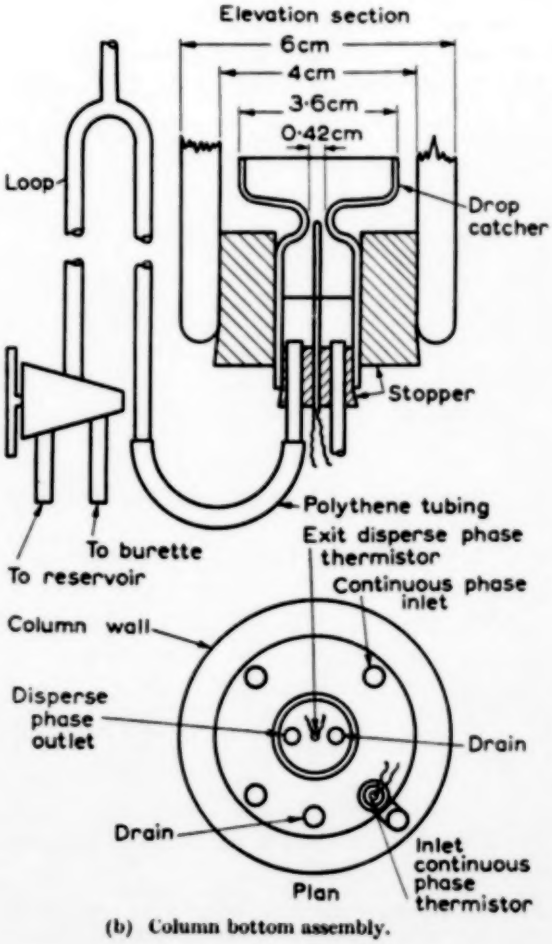
FIG. 5. Drag coefficients for mercury and bromobenzene drops compared with the behaviour of solid spheres.

phase were not distorted in passing through the liquid surface. Bromobenzene drops were however appreciably distorted and this fact led to the decision to form them below the continuous phase-surface.

FIG 6.
Apparatus for heat-transfer measurements.

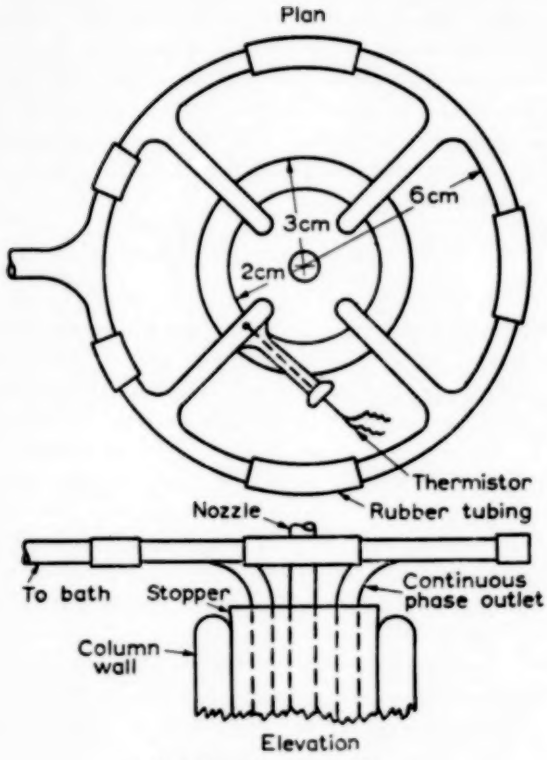


(a) Heat transfer apparatus.

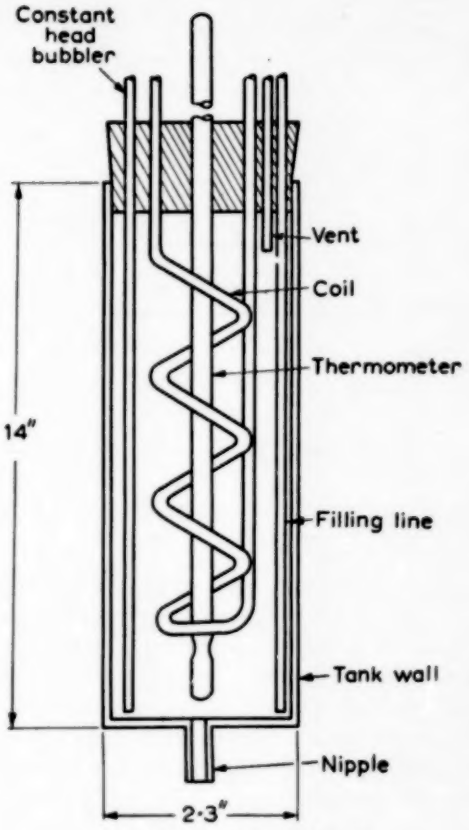


(b) Column bottom assembly.

FIG. 6 (*continued*)



(c) Column top assembly.



(d) Disperse phase feed tank.

The effect of wall proximity on the terminal drop velocity was also studied by using columns of varying diameter. It was found that the effect of column diameter had disappeared when the column diameter was about ten times that of the drop.

A column diameter of 3·71 cm was used in the heat-transfer work and the effect of wall proximity could be discounted.

Heat-transfer Measurement

A schematic diagram of the equipment used is shown in Fig. 6.

A vacuum-jacketed glass column was fed with the disperse phase from a constant head stainless-steel tank. The disperse phase was collected in an hourglass-shaped catcher at the base of the column and coalesced in the narrowest section where a thermistor was located. The level in the catcher was maintained constant by means of a "swinging-leg" interface control. The disperse-phase temperature in the feed tank was measured with a calibrated thermometer reading to 0·02°C.

The continuous phase reservoir consisted of a thermostat bath controlling to ± 0·02°C over the range 15°C to 30°C. The continuous phase was pumped from the thermostat in a loop through a calibrated rotameter, upwards through the column and back to the thermostat.

Temperatures were read by means of thermistors at the points indicated in Fig. 6. The thermistors could be switched in turn into a resistance network and enabled temperatures to be read with a precision of ± 0·02°C. The thermistors and thermometers were calibrated against a National Research Council of Canada standard thermometer. The thermistor bridge circuit is shown in Fig. 7. Thermistors were obtained from the

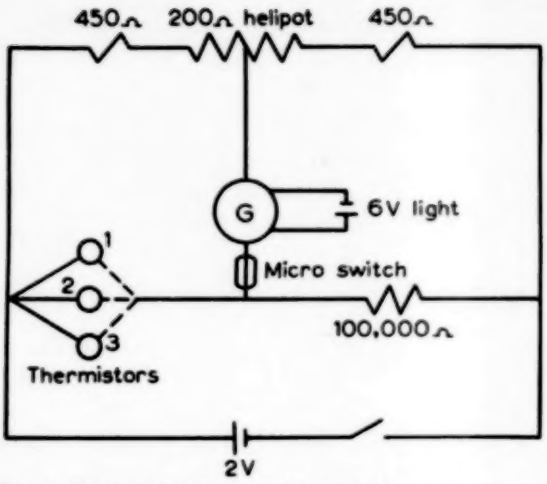


FIG. 7. Bridge circuit for use with thermistor temperature-measuring elements.

Victory Engineering Corporation, New Jersey (Veco type 51-A1 resistance at 25°C $\approx 10^5$ ohms) and showed excellent stability after pretreatment at 100°C for one month.

The effective column length was 20·5 cm in most of the runs. Temperature readings were taken after about half an hour of steady operation, the rotameter reading noted and drop sizes and velocities checked. The difference between the temperatures of the in- and out-flowing continuous phase was in no case greater than 0·03°C so that the continuous phase could be assumed to be at a constant temperature without sensible error. Care was taken to use a column length which would ensure an accurately measurable-temperature difference between the phases at the base of the column.

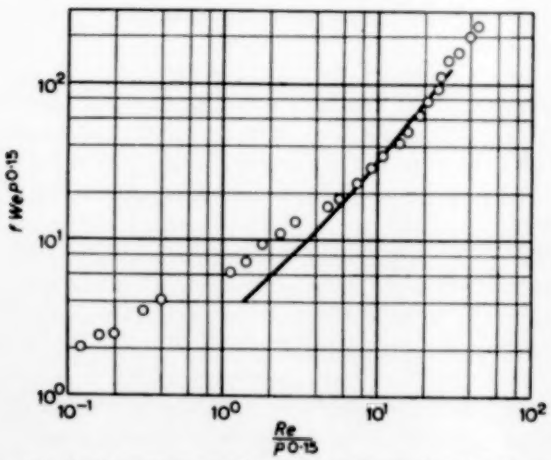
RESULTS AND DISCUSSION

Drag Coefficients

Experimental drag coefficients have been reported in Fig. 5 and show a deviation from solid-sphere behaviour only at Reynolds numbers above 200, when drop oscillation was observed to occur.

A visual study of the behaviour of bentonite clay particles suspended in the bromobenzene drops clearly revealed the fact that internal circulation was fully developed at Reynolds numbers well below 200, so that the effect of internal circulation on the drag coefficient, was too small to be detected.

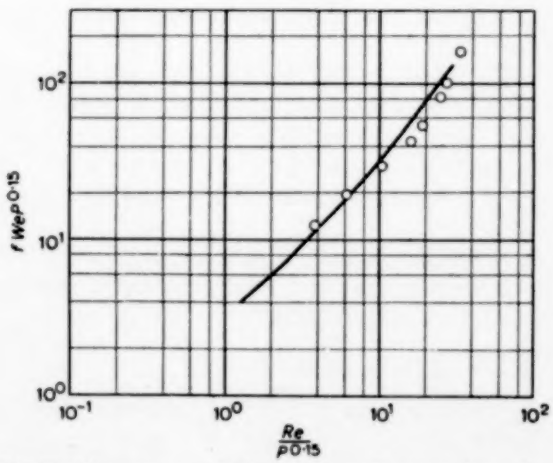
A comparison between the present results and the correlation suggested by HU and KINTNER [2] is made in Fig. 8. The latter workers established



(a) HU-KINTNER correlation for mercury drops in glycerol water solutions :

$$P = \frac{3}{4}\frac{Re^4}{f\,We^3}$$

——— HU-KINTNER data. ○ Present work.



(b) HU-KINTNER correlation for bromobenzene drops in glycerol-water.

$$P = \frac{3}{4}\frac{Re^4}{f\,We^3}$$

——— HU-KINTNER data. ○ Present work.

FIG. 8. Comparison between experimental results and the correlation of HU and KINTNER [2].

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a functional relationship between the drag coefficient and the Reynolds and Weber groups by dimensional analysis, and determined the exponents of the above groups by a trial and error fit of experimental data. It was thus found possible to correlate the data for falling liquid drops in water by means of a single line plotted on the co-ordinates shown in Fig. 8. From a comparison with the present work it is clear that the effect of continuous phase viscosity, not investigated by HU and KINTNER, is considerable and can lead to discrepancies when the field liquid is not pure water.

Continuous-Phase Heat-Transfer Coefficients

Values of the continuous-phase heat-transfer coefficient were calculated from the data obtained with mercury drops by means of equation (1). The continuous-phase temperature was taken as the average, the maximum change being 0·03°C. The heat loss from the mercury drop to the air during its formation was calculated to be insignificant. The heat loss at the coalescing section was not known but assumed to be insignificant as the contact area and driving force were both small. The continuous-phase velocity was taken as the average velocity of the fluid in the column. Although the continuous phase flow was laminar, a very flat velocity profile appeared to exist when the notion of suspended particles was observed under strong illumination. This appears to result fortuitously from the design of the entry and exit sections. Continuous-phase heat-transfer coefficients are plotted in Fig. 9 and compared with published results for heat transfer to solid spheres and the analogous situation of mass transfer to liquid drops where the dispersed-phase resistance is negligible. The range of the variables covered in the present work was:

$$Re - 0{\cdot}5 \text{ to } 3{,}000$$
$$Pr - 6 \text{ to } 3{,}300$$
$$Nu - 10 \text{ to } 120$$

It may be seen that the transfer coefficients for liquid drops depart from those found for solid spheres at a Reynolds number of about 200. As this point coincided with observed drop oscillation it is apparent that oscillation causes some boundary-layer degradation and an increased transfer coefficient.

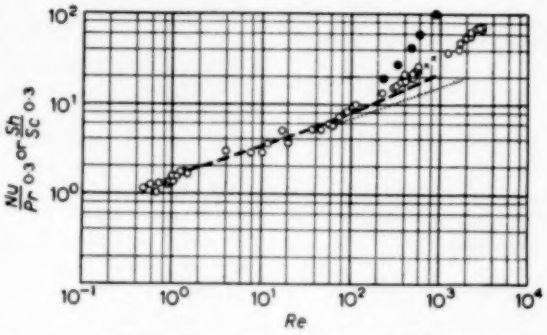

FIG. 9. Continuous phase heat transfer coefficient correlation from mercury drop data.
○ Exp. data.
— — — Curve from MCADAMS [3].
- - - - - - Data of TANG, *et al.* [28].
× Data of LICHT and PANSING [21].
● Data of COULSON and SKINNER [20].

Disperse-Phase Heat-Transfer Resistance

Experiments were performed using bromobenzene as the disperse phase under conditions which ensured that a large part of the overall resistance to heat transfer lay in the bromobenzene phase.

Corrections for heat transfer during drop formation were made as already explained (Fig. 3). This correction was found to be equivalent to a fractional approach to equilibrium due to drop formation of between 0·12 and 0·16 and is of the same order of magnitude as the equivalent results of LICHT and CONWAY [22] and HEERTJES *et al.* [11] which were between 0·18 and 0·20.

Values of the continuous-phase heat-transfer coefficient (h_c) were deduced from the results obtained using mercury drops (Fig. 9). From the parameter $\frac{h_c t}{C_{p_d} \cdot \rho_d \cdot r}$ and the experimental E_M values, the effective thermal conductivity of the drops was found by means of the modified GROBER chart shown in Fig. 2. The ratio of effective to molecular diffusivity (R) was then calculated.

A range of Reynolds numbers of from 10 to 600 was covered, results being shown in Table 1, together with those calculated from data in the literature.

Table 1. R values calculated from this work and from literature data.

Source of data	*System*	*R range*	*Re range*	*Type of drop behaviour*
GARWIN and SMITH [23]	Cold benzene drops rising in hot-water heat transfer	1·72–2·1	1500–1780	No drop oscillation
GARWIN and SMITH [23]	Hot benzene drops rising in cold-water heat transfer	1·6–2·4	730–810	No drop oscillation
McDOWELL and MYERS [24]	Cold kerosene drops rising in hot-water heat transfer	2·25	circa 2000*	No drop oscillation
McDOWELL and MYERS [24]	Cold xylene drops rising in hot-water heat transfer	2·25	circa 2400*	No drop oscillation
This work	Bromobenzene drops falling in hot or cold glycerol-water-solutions heat transfer	1·8–3·3	10–120	No drop oscillation
HEERTJES *et al.* [11]	Isobutanol drops rising in water-mass transfer of water	1·9–2·1	20–200	No drop oscillation
This work	Bromobenzene drops falling in hot or cold glycerol-water solutions heat transfer	7–12	315–620	Drop oscillations present
HUGHES and GILLILAND [25]	Water drops falling through carbon dioxide atmosphere-mass transfer of carbon dioxide	20	300–3000	Drop oscillations present
GARNER and SKELLAND [26]	Nitrobenzene drops containing acetic acid falling in water-mass transfer of acetic acid	6·5 10 21	270 370 480	Type of drop behaviour not stated by authors. Oscillations indicated by *R* values
PANSING [27]	Perchloroethylene drops containing acetic acid falling in water-mass transfer of acetic acid	25–53 40–61 50–71	375 595 700	Drop oscillations present, although oscillation decay indicated by range of *R* for constant conditions

* Exact continuous-phase temperature not given by authors; temperature of 170°F given in sample calculation of reference [24] was used to estimate the Reynolds number.

In the circulating régime R values found in this study varied from 1·8 to 3·3 a result in general agreement with corresponding figures calculated from literature data and supporting the value of $R = 2{\cdot}25$ deduced from the KRONIG and BRINK model.

In the oscillating régime, R values found here and deduced from published data are considerably higher than is found for circulation alone.

The constancy of R with column length, which was found, appears to disprove the hypothesis of oscillation decay advanced by HUGHES and GILLILAND [25] and gives strong support for the fundamental soundness of the use of an effective diffusivity to express the transfer resistance of the disperse phase.

A serious limitation of the present work is its failure to define the range of conditions over which circulation is present and the point at which oscillation starts. Much more experimental work is needed before this issue can be clarified.

CONCLUSIONS

The influence of internal circulation in liquid drops is to raise the effective diffusivity to a value equal to 2·25 times the molecular diffusivity.

No precise data is yet available to define the régime over which pure circulation occurs.

Oscillation causes the effective diffusivity to be greatly increased above the value obtained for pure circulation.

Existing correlations for the drag coefficients of liquid drops require to be extended to account for wider variations in the viscosity of the field liquid.

Internal circulation by itself has a small, and

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in this work unmeasurable, effect on the drag coefficient or the continuous-phase heat-transfer coefficient, the latter two quantities agreeing with solid-sphere behaviour.

Drop oscillation increases the drag coefficient, the continuous phase heat-transfer coefficient and the effective diffusivity within the drop. The latter effect is doubtless the manner in which "pulsed" columns achieve a superior performance.

Acknowledgements—One of us (I.J.O.K.) wishes to thank the National Research Council of Canada for financial assistance in the form of two studentships.

NOTATION

A_N = an eigenvalue.
C_{p_d} = specific heat of drop, cal/g°C.
d = drop diameter, cm.
D = mass diffusivity, cm²/sec.
e = base natural logarithms, dimensionless.
E = fractional approach to equilibrium, dimensionless.
E_F = fractional approach to equilibrium, during drop formation, dimensionless.
E_M = fractional approach to equilibrium during drop fall, dimensionless.
E_T = total fractional approach to equilibrium, dimensionless.
f = drag coefficient, dimensionless.
g = gravitational acceleration, 980 cm/sec².
h_c = continuous phase heat transfer coefficient, cal/cm² sec°C.
k = thermal conductivity, calcm/cm²sec°C.
L = column length, cm.
n = an integer, 1, 2, 3 . . . 00, dimensionless.
Nu = Nusselt number, hcd/k, dimensionless.
Pr = Prandtl number, $Cp\mu/k$, dimensionless.
r = drop radius, cm.
R = diffusivity or conductivity ratio, dimensionless.
Re = Reynolds number, $dv\rho/\mu$, dimensionless.
Sc = Schmidt number, $\mu/D\rho$, dimensionless.
Sh = Sherwood number, kd/D, dimensionless.
t = contact time, sec.
Tc = continuous phase temperature, °C.
Td = average temperature, of drop, °C.
Ti = average temperature of incoming drop, °C.
To = average temperature of outgoing drop, °C.
Vc = continuous phase velocity, cm/sec.
Vd = relative velocity between drop and continuous phase cm/sec.
α = thermal diffusivity, cm²/sec.
α_E = effective thermal diffusivity, cm²/sec.
π = 3·142.
ρ_c = continuous phase density, g/cm³.
ρ_d = disperse phase density, g/cm³.
μ_c = continuous phase viscosity, poise.
μ_n = an eigenvalue.

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APPENDIX

Continuous-Phase heat-transfer coefficient correlation.

Run number	*% glycerol by weight*	h_c *cal/cm²sec°C*	*Nu*	*Pr*	*Re*	$Nu/(Pr)^{0.3}$
1	0	0·455	70·0	8·04	1250	36·5
2	0	0·462	70·7	8·04	1250	37·8
3	0	0·474	77·0	8·04	1430	41·1
4	0	0·474	77·5	8·04	1430	41·5
5	0	0·484	87·4	7·21	1700	48·3
6	0	0·430	75·5	8·04	1670	40·4
7	0	0·482	90·2	5·45	2200	54·0
8	0	0·453	86·5	7·21	1680	47·8
9	0	0·479	91·6	7·28	1680	50·6
10	0	0·508	101	8·04	1930	53·9
11	0	0·496	98·8	7·21	1990	54·5
12	0	0·477	98·0	7·28	1960	54·1
13	0	0·473	98·0	7·21	1980	54·1
14	0	0·489	101	5·45	2600	68·8
15	0	0·476	104	7·21	2250	57·4
16	0	0·516	115	7·21	2250	63·2
17	0	0·510	115	8·04	2230	63·2
18	0	0·507	114	5·45	3000	68·5
19	0	0·536	120	5·75	2870	71·0
20	0	0·530	122	5·45	3000	73·0
21	52·5	0·198	46·1	44·1	285	14·4
22	52·5	0·203	47·2	40·0	310	15·6
23	52·5	0·202	52·0	40·7	345	17·1
24	52·5	0·178	45·1	64·2	215	12·9
25	52·5	0·231	64·0	43·1	380	20·6
26	52·5	0·199	54·2	40·8	400	17·8
27	52·5	0·210	65·5	40·7	470	21·5
28	52·5	0·180	56·0	40·6	470	18·4
29	52·5	0·186	63·9	42·1	485	20·8
30	52·5	0·200	69·1	41·5	495	22·6
31	74·7	0·0715	20·2	358	20·0	3·50
32	74·7	0·0894	24·9	197	47·5	5·10
33	74·7	0·0955	29·1	197	57·0	5·97
34	74·7	0·102	31·0	188	61·9	6·45
35	74·7	0·109	36·2	193	74·2	7·26
36	74·7	0·101	33·5	211	63·8	6·72
37	74·7	0·0821	30·8	366	36·5	5·29
38	74·7	0·106	39·5	190	93·0	8·17
39	74·7	0·111	45·7	197	105	9·37
40	74·7	0·113	46·5	188	113	9·67
41	87·5	0·0654	20·2	727	7·70	2·80
42	87·5	0·0627	20·9	695	10·2	2·94
43	87·5	0·0748	27·4	1450	3·80	3·09
44	87·5	0·0850	34·6	834	11·9	4·66
45	87·5	0·0842	38·0	762	16·7	5·21
46	97·8	0·0430	14·5	3340	0·58	1·27
47	97·8	0·0386	13·1	3720	0·49	1·11
48	97·8	0·0394	14·7	3300	0·72	1·29
49	97·8	0·0315	11·6	3420	0·68	1·01
50	97·8	0·0373	15·2	3340	0·93	1·33
51	97·8	0·0358	14·5	3380	0·91	1·26
52	97·8	0·0415	18·6	3740	1·00	1·57
53	97·8	0·0396	17·9	3370	1·15	1·57
54	97·8	0·0408	20·4	7310	1·25	1·74
55	97·8	0·0408	20·4	3500	1·38	1·77

Calculations for the bromobenzene-drops – glycerol-water-solutions heat-transfer experiments.

Run No.	μ_c poise	$f(Re)^2$	Re	h_c cal / cm² °C sec	$v_d - v_c$ cm/sec	t sec	$\frac{h_c d}{C_{p_d} d_d J}$	E_T	$1 - E_M$	$\frac{h_c r_d}{k_s}$	R
1	0·0258	$8·02 \times 10^4$	338	0·0993	17·0	0·365	0·452	0·524	0·433	10·4	7·95
2	0·0258	8·21	338	0·104	15·8	0·476	0·614	0·559	0·525	13·0	6·71
3	0·0260	8·65	350	0·105	15·8	1·04	1·33	0·762	0·283	11·6	7·76
4	0·0270	7·19	315	0·105	16·4	2·94	3·89	0·969	0·037	9·7	8·91
5	0·0272	8·30	340	0·0960	16·7	2·89	3·30	0·956	0·052	9·6	8·73
6	0·0272	8·33	340	0·102	16·8	4·28	5·17	0·976	0·029	13·4	6·69
7	0·0222	10·4	385	0·113	17·3	4·16	5·97	0·977	0·028	14·0	6·64
8	0·0222	19·0	530	0·116	19·8	0·313	0·377	0·476	0·624	13·4	8·66
9	0·0192	26·1	620	0·121	19·5	0·605	0·752	0·641	0·427	10·3	11·8
10	0·0260	15·0	465	0·110	18·4	0·891	0·986	0·720	0·333	9·9	12·0
11	0·0270	12·8	430	0·105	19·4	2·48	2·69	0·908	0·109	10·4	10·1
12	0·0270	14·7	460	0·103	19·4	2·48	2·54	0·893	0·127	12·0	9·02
13	0·0274	14·4	450	0·103	19·5	3·70	3·75	0·953	0·056	11·7	9·26
14	0·0274	13·3	440	0·102	18·2	3·96	4·11	0·938	0·073	15·1	7·00
15	0·102	$6·47 \times 10^3$	73	0·0503	11·7	0·530	0·296	0·390	0·718	21·8	2·16
16	0·102	6·50	74	0·0509	12·0	0·983	0·553	0·496	0·593	19·8	2·42
17	0·0991	7·29	80	0·0487	12·1	1·39	0·734	0·551	0·528	17·9	2·61
18	0·100	7·70	82·5	0·0500	12·3	3·93	2·08	0·749	0·295	21·9	2·24
19	0·100	7·67	82	0·0498	10·9	4·43	2·34	0·831	0·199	15·9	3·07
20	0·101	7·13	77·5	0·0508	12·0	6·03	3·30	0·869	0·154	19·3	2·54
21	0·101	6·61	74	0·0472	12·3	5·91	3·10	0·849	0·178	19·9	2·23
22	0·100	13·3	118	0·0526	14·5	0·428	0·198	0·336	0·781	20·8	2·99
23	0·100	11·1	106	0·0537	14·1	0·837	0·420	0·429	0·672	23·5	2·54
24	0·100	11·4	107	0·0541	13·8	1·22	0·610	0·521	0·563	18·6	3·26
25	0·100	12·3	112	0·0532	13·7	3·52	1·69	0·716	0·334	20·0	3·06
26	0·100	$1·27 \times 10^4$	115	0·0529	15·2	3·17	1·50	0·662	0·398	22·2	2·77
27	0·100	1·25	114	0·0530	14·6	4·94	2·35	0·776	0·263	21·9	2·80
28	0·100	1·32	118	0·0527	14·5	4·97	2·30	0·753	0·291	24·0	2·59
29	0·215	$1·93 \times 10^3$	31·5	0·0336	9·50	0·653	0·213	0·327	0·765	20·0	1·79
30	0·414	0·514	11·3	0·0272	6·06	1·54	0·408	0·467	0·606	11·9	2·45
31	0·424	0·538	11·8	0·0300	6·50	2·60	0·750	0·573	0·485	14·5	2·29
32	0·435	0·543	12·0	0·0274	6·54	7·38	1·87	0·838	0·184	10·8	2·87
33	0·435	0·545	12·0	0·0271	6·64	7·26	1·81	0·830	0·193	10·8	2·83
34	0·436	0·425	10·2	0·0283	6·30	11·5	3·34	0·910	0·102	14·7	1·94
35	0·439	0·484	10·8	0·0271	6·08	11·9	3·07	0·916	0·096	12·7	2·31
36	0·437	0·807	16·3	0·0264	7·98	0·777	0·165	0·312	0·782	14·6	2·34
37	0·437	0·788	16·1	0·0273	8·05	1·15	0·250	0·367	0·720	14·4	2·37
38	0·438	0·805	16·3	0·0268	7·88	2·13	0·455	0·465	0·608	16·5	2·06
39	0·434	0·858	17·3	0·0262	8·09	5·96	1·25	0·693	0·349	14·5	2·41
40	0·433	0·915	18·1	0·0265	8·59	5·61	1·14	0·668	0·377	15·0	2·33
41	0·435	0·782	16·0	0·0264	7·64	9·43	2·07	0·789	0·240	16·4	2·08
42	0·476	0·917	18·2	0·0266	8·80	8·18	1·77	0·831	0·192	10·7	3·05

NOTE : E_f values for the various continuous phases were : 28·7% $G - E_f = 0·160$; 56·5% $G - E_f = 0·150$; 74·3% $G - E_f = 0·120$.

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Distillation at minimum variable reflux

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Abstract—Minimum heat input in a distillation in which the reflux is variable is calculated by a modification of UNDERWOOD's minimum-reflux calculation. The method is based upon the analytical theory of distillation previously given by one of the authors. Instead of the molal liquid and vapour rates actually occurring in the column, generalized rates are defined which are dependent on the molal heat rates of the vapour phase and of the liquid phase. The equations between the generalized rates are formally identical with the equations between the molal rates in a distillation at constant reflux. To obtain these generalized rates the molal vapour heat content must be approximated by a linear function of the equilibrium constant of a reference component K and the molal liquid heat content must be approximated by a linear function of $\frac{1}{K}$. These approximations need, however, only be valid in the relatively narrow temperature range between the two "pinches." Constant relative volatilities have also to be assumed for that region only.

Résumé—Les auteurs présentent une méthode pour calculer la quantité minimum de chaleur nécessaire pour effectuer une distillation à reflux variable. La méthode est fondée tantôt sur la méthode d'UNDERWOOD pour calculer le reflux minimum en cas d'un reflux constant, tantôt sur la théorie analytique de la distillation développée antérieurement par un des auteurs. Au lieu des courants de vapeur et de liquide actuels on introduit des courtants généralisés qui dépendent des enthalpies de la vapeur et du liquide dans la colonne. Ces quantités généralisées sont liées les unes aux atures par des équations identiques formellement aux équations gouvernant la distillation à reflux constant. Pour obtenir ces quantités généralisées il faut admettres que l'enthalpie de la vapeur puisse être représentée par une fonction linéaire de la constante d'équilibre K d'un des composants du mélange, pris comme substance de référence ; il faut également que l'enthalpie du liquide puisse être représentée par une fonction linéaire de $\frac{1}{K}$. Il suffit que ces approximations soient valables entre les deux régions de composition invariable (pinches). Il faut aussi que les volatilités des composants aient un rapport constant dans cette intervalle de température seulement.

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OBJECT OF THE PAPER

UNDERWOOD's well-known method for the calculation of the minimum reflux ratio for distillations in which the components have a constant relative volatility and in which the reflux remains constant throughout the column is widely used at present [1, 3]. It does not seem to be generally known that the method can be generalized to calculate minimum reflux in a distillation in which the components still have a constant relative volatility but the reflux is variable.

In this paper the theoretical basis of the generalized method is given, and the theory is illustrated by an example. The discussion also explains why the assumption of a constant relative volatility still gives satisfactory results even in case of a large difference in temperature between top and bottom of a column.

UNDERWOOD'S METHOD

We may recall that in the simple case in which the distillation is carried out in such a way that only two components are present in specified quantities in both products, the distillate and the bottom product, the method consists in the calculation of a root common to two algebraic equations one pertaining to the top section, the other to the stripping section. The equations are*

$$\Sigma_i \frac{\alpha_i y_{i,D}}{\alpha_i - w} = R_D + 1 \qquad (1)$$

*A list of notations is given at the end of this paper.

for the top section and

$$\Sigma_i \frac{\alpha_i x_{i,B}}{\alpha_i - w} = -R_B \qquad (2)$$

for the stripping section.

Instead of using concentrations and the unknown w, the present authors prefer the use of molal rates and of the variable $t = w^{-1}$ as many of the calculations become simpler in that case. Equations 1 and 2 rewritten in molal rates and introducing t as the unknown variable become after some rearrangement :

$$\Sigma_i \frac{D_i}{1 - \alpha_i t} = -L_t \qquad (3)$$

$$\Sigma_i \frac{B_i}{1 - \alpha_i t} = L_b \qquad (4)$$

The condition of minimum reflux is that eqs. (3) and (4) have one common root which is thus also a root of the equation :

$$\Sigma_i \frac{F_i}{1 - \alpha_i t} = L_b - L_t \qquad (5)$$

This root is the one situated between the values α_h^{-1} and α_l^{-1} if h and l are used to denote the two "key components" that are specified in the distillate and in the bottom product. The index h refers to the heavy key, the index l to the light key $\alpha_h < \alpha_l$.

The difference $L_b - L$ depends on the heat content of the feed; it is equal to the liquid portion of the feed under feed tray conditions*.

Let $t = \Omega$ be the root of eq. (5) which satisfies the condition $\alpha_l^{-1} < \Omega < \alpha_h^{-1}$, then minimum reflux corresponds to the values of L_b or of L_t as calculated from eq. (3) and eq. (4) respectively with $t = \Omega$.

Variable reflux.

It has been shown by one of the present authors that the calculation of any distillation in which the reflux is variable but the relative volatilities are constant, can be reduced to a calculation of a distillation with constant reflux and constant α_i, provided that the molal heat content of the vapour and of the liquid can be approximated by a certain quadratic function of the equilibrium constant of the reference component [4, 5]. The reference component is the one for which $\alpha = 1$. Van Wijk and de Haas van Dorsser have discussed some specializations of the general expressions [6]. The proof that a distillation with variable reflux can be calculated as a distillation with constant reflux will now be repeated here for a special approximation of the molal heat content which was given in the last mentioned article. This approximation is used in the following example of calculation of minimum variable reflux.

Let us assume that the heat content per mole of liquid H_l and per mole of vapour H_v in the column are given by the expressions

$$H_l = H_l^{(0)} + H_l^{(1)}/K \qquad (6)$$

$$H_v = H_v^{(0)} + H_v^{(1)} K \qquad (7)$$

in which K is the equilibrium constant of the reference component and the H's in the right-hand sides are constants.

In a distillation with variable reflux the vapour and liquid streams have to satisfy the heat balance, which for the section B indicated in Fig. 1 has the form

$$H_B = H_{v,m} V_m - H_{l,m+1} L_{m+1}. \qquad (8)$$

Here V_m is the total molal vapour flow leaving the mth tray so $V_m = \Sigma_i V_{i,m}$ if $V_{i,m}$ denotes the molal vapour flow of component i. Similarly $L_{m+1} = \Sigma_i L_{i,m+1}$.

Substituting eqs. (6) and (7) in eq. (8) we obtain among others a term $K_m V_m$ and a term L_{m+1}/K_{m+1}. The former is equal to $\Sigma_i V_{i,m}/\alpha_i$ the latter is equal to $\Sigma_i L_{i,m+1} \alpha_i$. In fact denoting the absorption factor of the reference component on the mth tray by $A_m = L_m/V_m K_m$ and its reciprocal value by S_m (stripping factor) and remembering that the equilibrium relation on an ideal tray demands that $L_{i,m} = \alpha_i^{-1} A_m V_{i,m}$ we have

$$K_m V_m = K_m \frac{V_m}{L_m} \Sigma_i L_{i,m} = A_m^{-1} \Sigma_i \alpha_i^{-1} A_m V_{i,m}$$

$$= \Sigma_i V_{i,m}/\alpha_i;$$

*The difference $L_b - L_t$ is often calculated in a different way, i.e. from a heat balance over the column assuming constant reflux in both sections.

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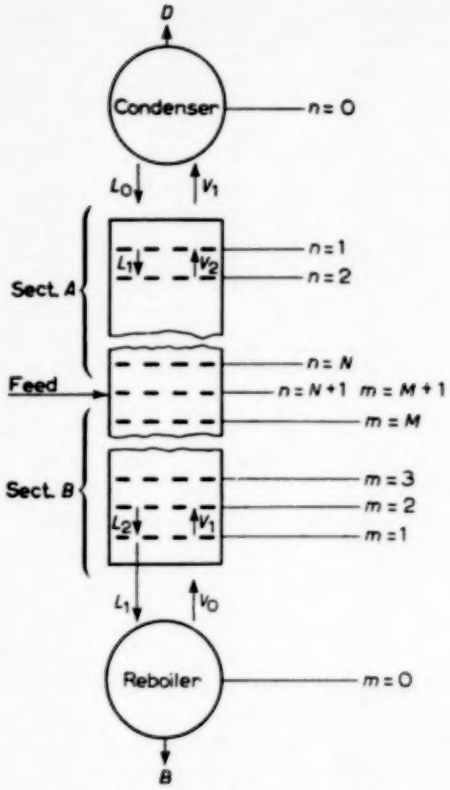

FIG. 1. Diagram showing the numbering of the trays in the two sections of a distillation column.

$$L_{m+1}/K_{m+1} = \frac{L_{m+1}}{K_{m+1}\,V_{m+1}}\,\Sigma_i\,V_{i,m+1} = A_{m+1}\,\Sigma_i\,\alpha_i S_{m+1}\,L_{i,m+1} = \Sigma_i\,\alpha_i L_{i,m+1}.$$

Thus eq. (8) can be written as :

$$H_B = H_0^{(0)}\,V_m + H_v^{(1)}\,\Sigma_i\,V_{i,m}/\alpha_i - H_l^{(0)}\,L_{m+1} - H_l^{(1)}\,\Sigma_i\,L_{i,m+1}\,\alpha_i \qquad (9)$$

in which K_m or K_{m+1} do not occur. Either one of the molal flows $V_{i,m}$ and $L_{i,m+1}$ can be expressed in the other one.

Eliminating for example $V_{i,m}$ by application of the relation $L_{i,m+1} = V_{i,m} + B_i$ one obtains

$$H_B = \Sigma_i\left[H_v^{(0)} - H_l^{(0)} + H_v^{(1)}/\alpha_i - H_l^{(1)}\,\alpha_i\right]\cdot L_{i,m+1} - \Sigma_i\left[H_v^{(0)} + H_v^{(1)}/\alpha_i\right]B_i. \qquad (10)$$

With

$$\Lambda_i = \left[H_v^{(0)} - H_l^{(0)} + H_v^{(1)}/\alpha_i - H_l^{(1)}\,\alpha_i\right] = \text{constant} \qquad (11)$$

we can rewrite (10) as

$$L_{(b)} = \Sigma_i \Lambda_i L_{i,m+1} = H_b + \Sigma_i\left[H_v^{(0)} + H_v^{(1)}/\alpha_i\right]B_i = \text{constant}. \qquad (12)$$

From the mathematical point of view eq. (12) is the condition for distillation at constant molal reflux of a mixture with "generalized" liquid flow rates, which are defined as

$$L_{(i,m+1)} = \Lambda_i\,L_{i,m+1}\,. \qquad (13)$$

Introducing the generalized residue rates

$$B_{(i)} = \Lambda_i\,B_i \qquad (14)$$

and the generalized vapour flow rates

$$V_{(i,m)} = \Lambda_i\,V_{i,m}. \qquad (15)$$

The equations expressing the conversation of matter

$$L_{i,m+1} = V_{i,m} + B_i \qquad (16)$$

hold also for the generalized components or

$$L_{(i,m+1)} = V_{(i,m)} + B_{(i)} \qquad (17)$$

as follows from eq. (16) by multiplication of both sides with the constant Λ_i. Eq. (12) is equivalent to eq. (8) which expresses the conservation of heat. Similarly from the equilibrium conditions

$$L_{i,m} = \alpha_i^{-1}\,A_m\,V_{i,m}, \qquad (18)$$

we obtain the generalized equilibrium conditions on multiplication by Λ_i

$$L_{(i,m)} = \alpha_i^{-1}\,A_m\,V_{(i,m)}. \qquad (19)$$

From eqs. (12), (17) and (19) it follows that a distillation at variable reflux can be treated mathematically as a distillation at constant reflux in which the generalized flow rates occur instead of the actual flow rates. The equation of conservation of matter and the equilibrium conditions, in which the actual relative volatilities, the actual absorption factors, and the actual stripping factors occur, are exactly equal to the corresponding relations in the actual distillation but the equation for the heat balance is based upon the validity of the expressions (6) and (7)

Table 1. *Separation Scheme of Six-component system**.

Component	*i*	*liq. feed*	*vap. feed*	F_i	B_i	D_i	α_i
Methane	1	0·010	0·250	0·260	—	0·260	20·6
Ethane	2	0·012	0·078	0·090	—	0·090	5·07
Propane	3	0·070	0·180	0·250	0·004	0·246	2·06
Butane	4	0·075	0·095	0·170	0·167	0·003	1·00
Pentane	5	0·072	0·038	0·110	0·110	—	0·429
Hexane	6	0·095	0·025	0·120	0·120	—	0·206
Total		0·334	0·666	1·000	0·401	0·509	

* The relative volatilities are average values estimated from different sources for a temperature of 83°C and a pressure of 20 atm.

for the molal heat content. If these expressions are valid the actual absorption factors are calculated from the distillation in which the generalized reflux is constant†.

A similar conclusion holds for the top section. The heat balance applied to the section *A* in Fig. 1 gives

$$H_D H_{v,n+1} V_{n+1} - H_{l,n} L_n. \qquad (20)$$

We can derive from eq. (20)

$$V_{(i)} = \Sigma_i V_{(i,n+1)} = H_D - \Sigma_i \left[H_l^{(0)} + H_l^{(1)} \alpha_i\right] D_i = \text{constant} \qquad (21)$$

(generalized equation of conservation of heat). In addition we have the equations

$$V_{(i,n+1)} = D_{(i)} + L_{(i,n)} \qquad (22)$$

(generalized equations of conservation of matter)

$$V_{(i,n)} = \alpha_i S_n L_{(i,n)} \qquad (23)$$

(generalized equilibrium conditions).

Consequently eqs. (3), (4) and (5), which result from eqs. (16) and (18) together with the condition of constant reflux $\Sigma_i L_{i,m} = \text{constant}$, are automatically also valid in terms of the generalized quantities (eqs. 15, 17 and 12). The theory of distillation using generalized quantities has been given in a previous communication to which reference is made for further details [4, 5].

Example of Calculation of Miniumum Constant Reflux

The theory will now be applied to a six component system which was previously discussed by Jenny [2]. Pressure 20 atmospheres, temperature of the feed 81°C. The component rates are in moles for one mole of feed. Propane is the light key component, butane is the heavy key; butane is chosen as the reference component.

For constant reflux we have $L_b = L_t + 0{\cdot}334$ and eq. (5) possesses the root $\Omega = 0{\cdot}719334$ which is in the range $\alpha_3^{-1} = 0{\cdot}485$ to $\alpha_4^{-1} = 1{\cdot}00$. This value of Ω inserted in eq. (3) gives the results $L_t = 0{\cdot}553$ and $L_b = 0{\cdot}887$ for minimum reflux conditions. These liquid rates correspond to a top reflux ratio $R_D = 0{\cdot}553/0{\cdot}599 = 0{\cdot}923$ and a vapour reflux ratio at the bottom $R_B = 1{\cdot}212$.

The Molal Enthalpies

The molal heat content of the liquid and of the vapour in the column must now be known.

For the calculation of the present example a constant specific heat of 0·6 kcal/kg has been assumed for the liquid. Thus if the liquid enthalpy is arbitrarily put equal to zero at $t = 0$°C and M is the molal weight,

†It is obviously incorrect to calculate the equilibrium constant of the reference component from the absorption factors inserting the generalized flow rates since by definition $A_m = \Sigma L_{i,m}/K\ \Sigma \alpha_i V_{i,m}$ and this is in general not equal to $\Sigma L_{(i,m)}/K\ \Sigma \alpha_i V_{(i,m)}$ for the same value of K.

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$$H_l = 0{\cdot}6\, t\, M. \qquad (24)$$

The molal enthalpy for the vapour is assumed to be

$$H_v = (0{\cdot}5\, t + 70)\, M. \qquad (25)$$

Both expressions are in kcal/kg mole and t is in degrees centigrade*).

The relation between the molecular weight of the two phases and the temperature or the equilibrium constant of the reference component must be obtained from a correlation. As such a correlation was not available for the present case the following procedure was used. The molecular weight is known at the top and at the bottom of the column; it is also known how the M of pure aliphatic hydrocarbons varies with their boiling temperatures under 20 atmospheres. The latter values were plotted as a function of the temperature and this graph was used to construct two similar curves almost parallel to the first one, on which the points corresponding to the terminal conditions are situated. The results of this procedure are given in Table 2 and are shown in graphical form in Fig. 3 as a function of K and of $1/K$

*As the object of this paper is to explain the method for calculation of a distillation with variable reflux rather than to calculate a given separation rigorously, the authors have not attempted to calculate the most accurate values for the heat contents involved.

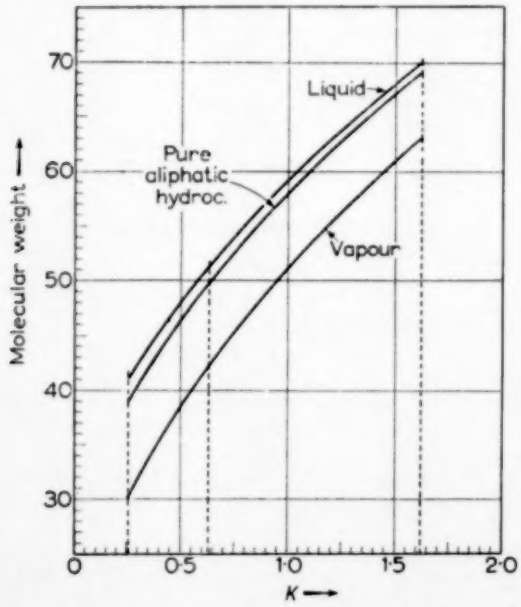

Fig. 2. Molecular weight as a function of the equilibrium constant of the reference component in the distillation of the six-component system. These molecular weights are used to convert enthalpy per unit of mass to molal enthalpy.

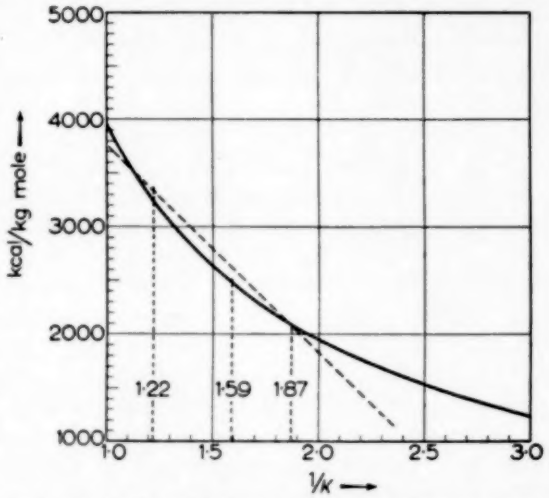

Fig. 3. Liquid molal heat content as a function of the reciprocal value of the equilibrium constant of the reference component. The straight line is the approximation of H_l between the two pinches used in the text. The dotted vertical lines indicate the values at the pinches and of the feed.

Table 2. Molal enthalpies of the liquid and of the vapour in the column as a function of the temperature or of K. (kcal/kg mole).

°C	K	m.w.liq.	H_l	m.w.vap.	H_v
36	0·255	41	885·6	30	2640
42·5	0·30	42·5	1084	32	2920
56	0·40	45·5	1529	35·5	3488
68	0·50	48	1958	38·5	4007
78	0·60	50·5	2363	41·5	4527
87	0·70	53	2767	44	4994
96	0·80	55	3168	46·5	5492
104	0·90	57	3557	49	5978
112	1·00	59	3965	51	6426
119	1·10	61	4355	53·5	6934
126	1·20	63	4763	55·5	7388
133	1·30	65	5187	57·5	7855
140	1·40	66·5	5586	59	8260
157	1·62	70	6594	61	9458

respectively. The molal heat of the vapour can excellently be represented by the expression of eq. (7), but the molal heat of the liquid must be approximated by different expressions of the type of eq. (6), each valid in a restricted range of temperatures only.

Minimum Variable Reflux

Underwood's relation is based upon the fact that an infinite number of trays is present in each section and that it is still possible to have one common tray in both sections which is the feed tray [3]. The composition of the terminal streams $V_{i,1}$ in the top and $L_{i,1}$ in the bottom is of no importance for the condition of minimum reflux and neither is the composition of the reflux. Since an infinite number of trays is present between the regions of invariant composition (pinches) and the feed tray in each section, it is sufficient to use eq. (6) for the molal liquid heat in the region of K values between the two pinches. Although the absorption factor of the reference component is approximately known beforehand in both pinches, the K values can only be calculated from them after the value of minimum reflux has been found.* Thus one has to select a certain interval of K values more or less arbitrarily, and adapt the constants in eq. (6). Afterwards it must be verified whether the K values at the pinches are actually situated in that interval.

A value $K = 0{\cdot}63$ or $1/K = 1{\cdot}59$ corresponds to the degree of vaporization of the feed. The straight line in Fig. 3 has been drawn such that

*In the theory set forth in ref. (5), it has been shown that in the stripping section of a column the product of absorption factors up to and including that of the mth tray, $Ap\,(m)$, is equal to the coefficient of t^m in the development of the following expression into a power series in t

$$\mathbf{A} = \frac{\Sigma_i\, V_{i(i,0)}/(1 - \alpha_i\, t)}{L_{(b)} - \Sigma_i\, B_{(i)}/(1 - \alpha_i t)}$$

The product of absorption factors is defined as

$$Ap\,(m) = A_1\, A_2\, A_3 \ldots . A_m$$

The above expression can be expanded into elementary rational fractions, so that one may write

$$\mathbf{A} = \Sigma_i \frac{c_i}{1 - \phi_i\, t}$$

in which ϕ_i^{-1} is a root of eq. (4) (for generalized quantities) and c_i is the residue of the function A if t approaches ϕ_i^{-1} or

$$c_i = \lim_{t=\phi_i^{-1}} \mathbf{A}\,(1 - \phi_i\, t).$$

Several conventional methods exist for the calculation of the residues, but we shall not discuss them now. The absorption factor product at the mth tray is thus

$$Ap\,(m) = \Sigma_i\, c_i\, \phi_i^{\,m}.$$

The absorption factor $A_m = Ap\,(m)/Ap\,(m-1)$ according to the definition of $Ap\,(m)$.

Since in the column section below the pinches (inclusive), the unspecified components do not appear, eq. (4) does not contain the components 1 and 2 and the maximum α occurring in that equation is $\alpha_3 = 2{\cdot}06$. The largest ϕ found from that restricted equation is obviously equal to the absorption factor of the reference component in the lower pinch, since it is the limiting value of

$$A_m = \frac{\Sigma_i\, c_i\, \phi_i^{\,m}}{\Sigma_i\, c_i\, \phi_i^{\,m-1}} \sim \phi_{\max} \text{ for } m \text{ approaching infinity.}$$

This ϕ depends on the value of R_B. However, in the present case, B_3 is a small fraction of $\Sigma_i\, B_{(i)}$ which, as can be shown from a discussion of eq. (4), has the consequence that one root is close to α_3^{-1}. This is the largest root and therefore the absorption factor in the pinch is close to α_3, since $\phi_{\max}$ is equal to the reciprocal value of the smallest root.

In the top section the theory shows that the function :

$$\mathbf{S} = 1 + Ap\,(1)^{-1}\, t + Ap\,(2)^{-1}\, t^2 + \ldots\, Ap\,(n)^{-2}\, t^n + \ldots$$

takes the place of the function A in the stripping section, and one obtains the analytical expression

$$\mathbf{S} = \frac{\Sigma_i\, L_{(i,0)}/(1 - \alpha_i^{-1}\, t)}{V_{(t)} - \Sigma_i\, D_{(i)}/(1 - \alpha_i^{-1}\, t)}.$$

Or expanding into elementary rational fractions

$$\mathbf{S} = \Sigma_i \frac{c'}{(1 - \phi_i'\, t)}$$

from which follows that

$$Ap\,(n)^{-1} = \Sigma_i\, c_i'\, (\phi_i')^n.$$

The ϕ_i''s are the reciprocal values of the roots of the denominator in the first analytical expression of $\mathbf{S}$ and the c_i''s are the residues of that expression for $t = (\phi_i')^{-1}$.

If the unspecified components in the top section 5 and 6 are ignored the largest value of ϕ_i' corresponds to the smallest root of the restricted equation. This root is somewhat smaller than 1·00 in the present case, owing to the fact that $D_{(4)}$ is a small fraction of $\Sigma_i\, D_{(i)}$. Since one has in the pinch of the top section

$$S_{\text{pinch}} = \lim_{n=\infty} \frac{Ap\,(n-1)}{Ap\,(n)} \sim \phi'_{\max},$$

the stripping factor in this pinch is somewhat higher than one.

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Table 3. Constants for calculating generalized rates.

i	A_i	$B_{(i)}$	$D_{(i)}$	$[H_v^{(0)} + H_v^{(1)}/\alpha_i]\, B_i$	$[H_l^{(0)} + H_l^{(1)}\,\alpha_i]\, D_i$
1	35670	—	9274	—	− 8833
2	6509	—	585·8	—	− 366.9
3	2139	8·556	526·2	15·42	+ 422·4
4	2640	440·9	7·920	1068	+ 11·27
5	8116	892·8	—	1427	—
6	20152	2418	—	3053	—
		3760·3	10394	5563	− 8767

A_i is defined by eq. (11), $B_{(i)}$ and $D_{(i)}$ by eq. (14) and as $A_i\ B_i$ and $A_i\ D_i$ respectively.

it differs less than 10 per cent from the molal liquid heat in the range of $1/K$ values 0·95 to 2·05. The constants in the right-hand sides of eqs. (6) and (7) have been calculated from this line for the liquid and from the corresponding graph for the vapour, giving the equations

$$H_l = 5683 - 1925/K \qquad (26)$$

$$H_v = 1458 + 4940\,K \qquad (27)$$

The resulting coefficients A_i are given in Table 3 together with other data necessary for the calculation of minimum reflux.

Returning now to eq. (5) we insert $F_{(i)} = B_{(i)} + D_{(i)}$ instead of F_i and instead of $L_b - L$ the expression

$$L_{(b)} - L_{(t)} = L_{(b)} - V_{(t)} + \Sigma_i\, D_{(i)} = H_B - H_D + \Sigma_i \left[H_l^{(0)} + H_l^{(1)}\,\alpha_i\right] D_i + \Sigma_i \left[H_v^{(0)} + H_v^{(1)}/\alpha_i\right] B_i + \Sigma_i\, D_{(i)}.$$

The constants H_B and H_D are the net upwards heat flows in the stripping section and in the top section respectively. The difference $H_B - H_D$ is, ignoring heat loss, equal to minus the heat introduced per mole of feed, or $-0{\cdot}334 \times 2480 - 0{\cdot}666 \times 4660 = -3932$ k cal/kg mole. Thus

$$L_{(b)} - L_{(t)} = -3932 - 8767 + 5563 + 10394 = 3250.$$

The root of eq. (5) which lies between $\alpha_b^{-1} = 1$ and $\alpha_l^{-1} = 0{\cdot}485$ has a value $= \Omega = 0{\cdot}684912$. If this root is inserted in eq. (4) in which the generalized residue rates $B_{(i)}$ are substituted a value $L_{(b)} = 5458$ is found at minimum reflux and from this follows $L_{(t)} = 5458 - 3258 = 2200$. The net upward heat fluxes in the column are now found from eqs. (12) and (21). One obtains recalling that $V_{(t)} = L_{(t)} + \sum_i D_{(i)}$:

$$H_B = 5458 - 5563 = -105 \qquad (29)$$

$$H_D = 2200 + 10394 - 8767 = +3827 \qquad (30)$$

These values represent the net upward heat flux at minimum variable reflux. They characterize the separation just so as the value of minimum reflux characterizes a separation in which the reflux is constant. They are constant in the entire column and also valid outside the range of validity of eq. (26). Thus H_B is the difference between the heat content in the vapour returned to the column from the reboiler V_0 and the heat content of the liquid flowing down from the lowest tray, L_1. Similarly H_D is the difference between the heat content of the vapour from the upper tray and that of the liquid reflux at the top of the column.

Reflux Ratio's at Column Terminals

The reflux ratio's at the top and at the bottom are now calculated assuming equilibrium condensation and vaporization respectively. The compositions of the liquid reflux from the condenser and of the vapour reflux from the reboiler are given in Table 4.

For the determination of the reflux ratio R_b the molal vapour reflux V_0 must be known.

Table 4. Reflux compositions for equilibrium in the reboiler and in the condenser.

comp. i	$\alpha_i B_i$	D_i/α_i	y_{iB}	x_{iD}
1	—	0·0126	—	0·082
2	—	0·0177	—	0·116
3	0·0082	0·1190	0·033	0·782
4	0·1670	0·0030	0·676	0·020
5	0·0472	—	0·191	—
6	0·0247	—	0·100	—
	0·2471	0·1523	1·000	1·000

The concentration of comp. i in the vapour reflux is $y_{iB} = \alpha_i B_i K/_{0·401}$ with K the equilibrium constant of the reference component in the reboiler; as $\Sigma y_{iB} = 1·00$ one has $K = 1·62$. Similarly $x_{iD} = D_i/\alpha_i K \times 0·599$ and $K = 0·255$ in the condenser.

It is calculated by solving eqs. (16) and (8) substituting $H_B = -105$ subject to the condition that K_1 at the lowest tray ($m = 1$) must have such a value that the liquid from this tray is at its boiling point or

$$\Sigma_i \left[V_0 \alpha_i y_{iB} + B_i \alpha_i\right] K_1 = V_0 + \Sigma B = L_1$$

The set of values $K_1 = 1·34$ and $V_0 = 0·517$ is found to satisfy these conditions, resulting in

$$R_B = 0·517/0·401 = 1·29 \qquad (31)$$

This is nearly equal to R_B for constant reflux.

In the top section, three similar conditions must be satisfied viz. eq. (20) with $H_D = 3827$, eq. (22) for ordinary i.e. nongeneralized flowrates and the condition that V_1 is at dew temperature. One obtains K (for $n = 1$) $= 0·0375$ and $L_0 = 0·750$ resulting in

$$R_D = 0·750/0·599 = 1·26. \qquad (32)$$

This is a considerable difference with $R_D = 0·923$ for constant reflux.

In a distillation with variable reflux the reflux ratio itself is, however, not a characteristic quantity; instead of it enter the net heat fluxes in both sections in the column, which are coupled through the heat input in the feed and through possibly occurring heat losses.

Equilibrium Constant at the "Pinch"

The temperatures in the regions of invariant composition, "pinches," are now calculated. It is necessary that both temperatures fall within the range of applicability of eq. (26). In the region of invariant composition the temperature remains constant, and thus the vapour heat and the liquid heat in eq. (8) or in eq. (20) have to be taken at equal values of K in each equation. The stripping factor of the reference component in the pinch of the stripping section is approximately equal to the smallest root in eq. (4) ignoring unspecified components and using generalized flow rates. The stripping factor in the pinch of the top section is equal to the greatest root occurring in eq. (3), if again unspecified components are ignored and generalized quantities are inserted. Thus one has exactly two equations to determine the total liquid or vapour rate and the equilibrium constant of the reference component for each "pinch." For instance in the top section one obtains with $L_{(l)} = 2200$ a value 1·0072 for the greatest root of eq. (3), thus $KV/L = 1·0072$ and eq. (20) becomes

$$3827 = \left[H_v(K) - H_l(K)\right] V + \\ + H_l(K) \times 0·599. \qquad (33)$$

The two equations are solved by trial and error. A value of K is assumed and the molal heats are calculated from the expressions (26) and (27). The vapour rate V resulting from eq. (33) is then inserted in the stripping factor together with $L = V - 0·599$. One obtains $K = 0·536$ or $1/K = 1·867$ and $V = 1·28$. By the corresponding procedure for the stripping section one obtains $K = 0·820$, or $1/K = 1·22$ and $V = 0·567$. The stripping factor of the reference component in the pinch of the stripping section is the smallest root in eq. (4) inserting $L_{(b)} = 5458$; it is 0·489.

The values of K corresponding to the invariant compositions are apparently both well within the range of validity of eq. (26), (cf. Fig. 3).

Since the calculation of minimum heat flux is based upon the fact that and infinite number of trays between the two pinches is present, the relative volatilities of the components in

the range of temperatures between the two pinches are only essential. A large variation of α_i outside this region does not affect the conclusions at all.

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NOTATION

$\mathbf{A}$ = function of a variable t defined by the relation $\mathbf{A} = 1 + Ap(1)\,t + Ap(2)\,t^2 + \ldots . Ap(m)\,t^m + \ldots .$

A_m = absorption factor of the reference component $A = \dfrac{L}{KV}$ on tray number m.

$A_{i,m}$ = absorption factor of component i on tray number m.

$Ap(m)$ = absorption factor product for the reference component at tray number m $Ap(m) = A_1 A_2 \ldots . A_m$.

α_i = relative volatility of component i in respect to the reference component $\alpha_i = K_i/K$.

B_i = residue rate of component i.

$B_{(i)}$ = generalized residue rate of component i, defined as $B_{(i)} = \Lambda_i B_i$.

b = subscript referring to the bottom section.

c_i = constant occurring in the expression of the absorption factor product $Ap(m) = \Sigma_i c_i \phi_i^m$.

D_i = distillate rate of component i.

$D_{(i)}$ = generalized distillate rate of component i, defined as $D_{(i)} = \Lambda_i D_i$.

F_i = feed of component i . $F_i = D_i + B_i$.

ϕ_i = reciprocal root of denominator in the analytic expression of $\mathbf{A}$. One has $Ap(m) = \Sigma_i c_i \phi_i^m$.

H_B = net upward heat flux in bottom section.

H_D = net upward heat flux in top section.

H_l = molal liquid heat content.

$H_l^{(0)}, H_l^{(1)}$ = constants occurring in the expression of molal liquid heat content as a linear function of $\dfrac{1}{K}$.

H_v = molal vapour heat content.

$H_v^{(0)}, H_v^{(1)}$ = constants occurring in the expression of molal vapour heat content as a linear function of K.

h = subscript to indicate heavy key.

i = subscript to indicate a component.

K = equilibrium constant of the reference component.

K_m = value of K on tray m.

$K_{i,m}$ = equilibrium constant of component i on tray m.

L_b = total liquid rate in bottom section.

$L_{(b)}$ = total generalized liquid rate in bottom section.

$L_{i,m}, L_{i,n}$ = liquid rate of component i from tray m or n respectively.

$L_{(i,m)}, L_{(i,n)}$ = generalized liquid rate of component i from tray m or n respectively.

L_m, L_n = total liquid rate from tray m or n respectively.

L_t = total liquid rate in top section.

$L_{(t)}$ = total generalized liquid rate in top section.

l = subscript indicating light key.

Λ_i = factor defined by the relation. $H_v^{(0)} - H_l^{(0)} + H_v^{(1)}/\alpha_i - H_l^{(1)}\,\alpha_i$. The component rates are transformed into generalized rates by multiplication by Λ_i.

M = molecular weight.

m = index for tray number in bottom section.

n = index for tray number in top section.

R_D = reflux ratio in condenser.

R_B = vapour reflux ratio in reboiler.

S_m, S_n = stripping factor of the reference component on tray m or n respectively.

Σ_i = sommation over all components.

t = mathematical variable used in the calculation of the absorption factor product.

t = temperature.

V_m, V_n = total vapour rate from tray m or n respectively.

$V_{i,m}, V_{i,n}$ = vapour rate of component i from tray m or n respectively.

$V_{(i,m)}, V_{(i,n)}$ = generalized vapour rate of component i from tray m or n respectively.

$V_{(t)}$ = generalized total vapour rate in top section.

w = mathematical variable occurring in the equations for calculation of minimum reflux.

$x_{i,B}$ = molal concentration of component i in liquid residue.

$y_{i,D}$ = molal concentration of component i in gaseous distillate.

Ω = characteristic root occurring in the equations for calculation of minimum reflux.

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Boundary conditions of flow reactor

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Abstract—An analysis is presented of the boundary conditions for a steady-state flow reactor with axial diffusion and first order reaction. Conclusions regarding reactor properties are reached as the result of simultaneous solution of the three differential equations for the reaction section, fore and after sections. Axial diffusion may occur in the latter two sections. The limits of behaviour, represented by a plug-flow reactor without diffusivity, and a fully-stirred reactor, are dissussed. Contributions of the diffusivities in the three parts of the system to the course of reaction in space are considered.

Résumé—Les auteurs présentent une analyse des conditions limites pour un réacteur à écoulement stationnaire avec diffusion axiale et une réaction de premier ordre. Leurs conclusions concernant les propriétés de réacteur sont le résultat de la solution simultanée de trois équations différentielles concernant la section principale de réaction, la section d'entrée et la section de sortie. La diffusion axiale peut intervenir aussi bien dans ces deux sections que dans la section principale. Ils discutent les limites de comportement correspondant d'une part aux réacteurs à piston sans diffusivité et d'autre part aux réacteurs à agitation parfaite. Ils considèrent l'influence propre sur le progrès de la réaction dans l'espace, de la diffusion dans les trois sections du réacteur.

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THE analysis of a plug flow chemical reactor which includes disappearance of a substance by chemical reaction and its transport in the axial direction by means of diffusional processes is of interest. The diffusional mechanisms may be molecular or turbulent. In the limit of infinitely large diffusivity the solution of this problem is identical with that of a fully-agitated chemical reactor. With zero diffusivity, the solution approaches that for a plug flow reactor, the type of reactor frequently assumed to be valid in purely chemical studies.

Two previous papers dealing with the problem are by DANCKWERTS [1] and HULBURT [2]. Present work discusses mathematical conclusions that result from the choice of different sets of boundary conditions.

The steady state differential equation in dimensionless form is :

$$\frac{1}{Pe}\frac{d^2f(z)}{dz^2} - \frac{df(z)}{dz} - Rf(z) = 0 \qquad (1)$$

where the Peclet group, $Pe = \frac{Lu}{D}$. L is a length term that characterizes the system, here taken for convenience as the bed length. Differently defined Peclet groups may be introduced if desired, using appropriate ratios of characteristic length terms. R is the rate group for a first order reaction $\frac{kL}{u}$, and f is the fraction of reactant remaining. It is assumed that there is no volume change during reaction. z is a dimensionless distance in the axial direction varying between $z = 0$ and $z = 1$.

DANCKWERTS [1] used the boundary conditions:

$$\text{a.} \quad f(0-) = 1 = f(0+) - \frac{1}{Pe}\frac{df}{dz}(0+) \qquad (2)$$

$$\text{b.} \quad \frac{df}{dz}(1) = 0 \qquad (3)$$

where $f(0-)$ in equation (2) represents the fraction remaining in the feed stream as it approaches the bed entrance, $f(0+)$, just

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within the bed entrance. The difference between these two values arises because of diffusion within the bed, represented by the third term. There is a discontinuity at this boundary as reported which will be shown later to be not necessarily correct. The second boundary condition was established on intuitive grounds.

HULBURT (2) employed the following set of boundary conditions:

a. $f(0-) = f(0+) = 1$ (4)

b. Same as equation (3).

Equation (4) neglects the diffusion directly within the reactor.

The solutions resulting from the choice of boundary conditions between these two authors differ by a constant factor $f(0)$ defined in equation (22) of this paper.

In considering a flow reactor it seems desirable not to neglect the role of the fore and after sections. In the present model these two end sections (Fig. 1) stretch from $-\infty$ to $+\infty$. The reactor bed is situated between 0 to 1 on the dimensionless z co-ordinate. This method

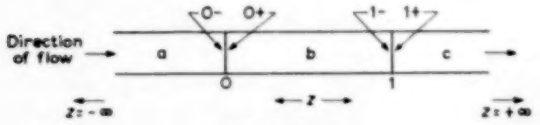

FIG. 1.

of treatment introduces boundary conditions at $z = \pm\infty$ which seem to be intuitively acceptable. In turn, the boundary conditions at $z = 0, 1$ are clarified by means of the behaviour of the solutions of the differential equations in the fore and after sections.

The differential equations for the three sections are:

$$\frac{1}{Pe_a}\frac{d^2f}{dz^2} - \frac{df}{dz} = 0 \qquad z \leqslant 0 \tag{5}$$

$$\frac{1}{Pe_b}\frac{d^2f}{dz^2} - \frac{df}{dz} - Rf = 0 \qquad 0 \leqslant z \leqslant 1 \tag{6}$$

$$\frac{1}{Pe_c}\frac{d^2f}{dz^2} - \frac{df}{dz} = 0 \qquad z \geqslant 1 \tag{7}$$

The Pe groups may differ between sections for reasons of velocity, presence of particles and the like.

The six required boundary conditions are:

(a) $$f(-\infty) = 1 \tag{8}$$

$$u_a A_a \left[f(0-) - \frac{1}{Pe_a}\frac{df}{dz}(0-)\right] = u_b A_b \left[f(0+) - \frac{1}{Pe_b}\frac{df}{dz}(0+)\right] \tag{9}$$

The total continuity equation states:

$$u_a A_a = u_b A_b = u_c A_c. \tag{10}$$

The use of the continuity condition permits simplification of the boundary condition for section a, equation (9) becoming:

(b) $$f(0-) - \frac{1}{Pe_a}\frac{df(0-)}{dz} = f(0+) - \frac{1}{Pe_b}\frac{df(0+)}{dz} \tag{11}$$

(c) $$f(0-) = f(0+) \tag{12}$$

(d) $$f(1-) - \frac{1}{Pe_b}\frac{df(1-)}{dz} = f(1+) - \frac{1}{Pe_c}\frac{df}{dz}(1+) \tag{13}$$

(e) $$f(1-) = f(1+) \tag{14}$$

(f) $f(\infty)$ is finite. (15)

Conditions (b) and (d) result from the conservation of reactants at exit and entrance of the bed, taking into account flow and diffusion.

Conditions (c) and (e) arise from the intuitive argument that at steady state the concentration should be continuous between sections at the bed entrance and exit.

The general solutions for the three sections containing the arbitrary constants, N_i, and obtained by solving equations (5), (6) and (7) are:

$$f = N_1 + N_2 \exp Pe_a z \qquad z \leqslant 0 \tag{16}$$

$$f = N_3 \exp\frac{Pe_b}{2}(1+a)z + N_4 \exp\frac{Pe_b}{2}(1-a)z \qquad 0 \leqslant z \leqslant 1 \tag{17}$$

$$f = N_5 + N_6 \exp Pe_c z \qquad z \geqslant 1 \tag{18}$$

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After inserting boundary conditions the complete solutions for the previous equations are:

$$\frac{1-f}{1-f(0)} = \exp(Pe_a z) \qquad z \leqslant 0 \quad (19)$$

$$f = g_0 \exp\left(\frac{Pe_b z}{2}\right)\left\{(1+a)\exp\left(\frac{a\,Pe_b(1-z)}{2}\right) - (1-a)\exp\left(\frac{a\,Pe_b(z-1)}{2}\right)\right\}, \quad 0 \leqslant z \leqslant 1 \quad (20)$$

and

$$f = f(1) = 2ag_0\exp(Pe_b/2) = \text{constant}, \quad z > 1 \quad (21)$$

where, $a = \sqrt{1 + 4R/Pe_b}$,

$$g_0 = \frac{2}{(1+a)^2\exp\left(\frac{aPe_b}{2}\right) - (1-a)^2\exp\left(-\frac{aPe_b}{2}\right)}$$

and

$$f(0) = g_0\left\{(1+a)\exp\left(\frac{aPe_b}{2}\right) - (1-a)\exp\left(-\frac{aPe_b}{2}\right)\right\} \quad (22)$$

In comparing the solutions for the three sections of the bed it is interesting to observe first that the $f - z$ profile in the fore section (a) depends upon the (a) – (b) boundary concentration, $f(0)$, which in turn depends in its absolute value upon the parameters in the reaction section, Pe_b and R. However, the profile in the centre reaction section (see equation 20) does not depend upon conditions in the fore section (a). The flat profile in the third section (equation 21) is the result of setting constant N_0 in the general equation (18) equal to zero in order to satisfy the boundary condition in equation (15). The level of concentration, $f(z > 1)$ in this section depends upon reaction and diffusion in the centre section. The value of the diffusivity in the after section does not enter into the results.

It now becomes of interest to discuss the boundary between sections (a) and (b). The following are pertinent points:

1. The value of the flux in the fore section is constant at a value of 1·0 which may be shown by substituting into the expression for the total flux, $f(z) - \frac{1}{Pe_a}\frac{df(z)}{dz}$, the solution for the section, equation (19). This finding remains true at the boundary, equation (11).

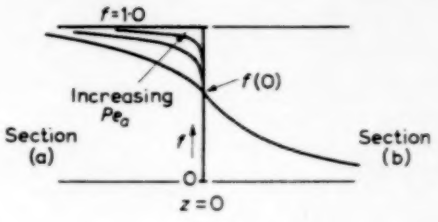

Fig. 2.

2. For $f(z < 0)$ the curve has the general shape as shown in Fig. 2. Thus as the Peclet group is caused to assume very large values, approaching conditions of zero diffusivity, the profile in section (a) approaches a step function (Fig. 2). Pertinent compositions and gradients at $f(0)$ are indicated in Fig. 3.

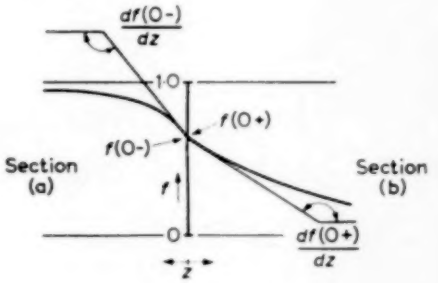

Fig. 3.

The solution for the reaction section (equation 20) is identical with that of Danckwerts. Both Danckwerts and the present authors used a value of unity for the flux at the inlet boundary. However in the present instance this value was established from an analysis of the fore section. The boundary condition as written by Danckwerts is the equivalent of the step function mentioned above since he did not include the term $\frac{1}{Pe_a}\frac{df(z<0)}{dz}$. The boundary conditions between the reaction and after section also were the same in the present work as that of Danckwerts.

Let us consider now the argument by which a zero gradient at the end of the reaction section is the logical limit. The solution for section c, equation (21) yielded a flat profile. Thus, in the boundary condition equation (13) the last term

is zero. Using also equation (14), it follows immediately that $\frac{df(1-)}{dz} = 0$. In effect, the boundary condition at $z = +\infty$ is drawn to the end of the reaction bed.

An additional feature of interest regarding the gradient at $z = 1$ is the rationalization between the above result, namely that $\frac{df(1-)}{dz} = 0$, and the conclusion that stems from consideration of a reaction with plug flow but without diffusion. In this latter case the differential equation is as follows :

$$\frac{df}{dz} = -Rf \qquad (23)$$

From the well-known solution of this equation, f may achieve a value of zero only at infinite bed length. At the finite bed length, $z = 1$,

$$\frac{df}{dz} = -R\exp(-R) \qquad (24)$$

This apparent conflict in boundary gradients for solutions with and without diffusion may be resolved by examination of the derivative of equation (20), which is as follows :

$$\frac{df}{dz} = \frac{-4R\left(\exp\frac{Pe_b(1-a)z}{2}\right)\{1-\exp(aPe_b(z-1)\}}{(1+a)^2-(a-1)^2\exp(-aPe_b)} \qquad (25)$$

Equation (24) for reaction without diffusion arises as $Pe_b \to \infty$ in equation (25). This limit must be taken within the bed, $0 < z < 1$. Then as $z \to 1$, $\left|\frac{df}{dz}\right| > 0$.

For any finite value of diffusivity, i.e., $Pe_b < \infty$, as $z \to 1$, $\frac{df}{dz} = 0$. The key term in this development is $\{1 - \exp(a\,Pe_b(z-1)\}$.

Fig. 4 portrays concentration profiles through the three sections of the reactor for selected values of Pe and R. The logical limits of plug flow reaction without diffusion ($Pe_b = \infty$) and of infinite diffusivity as with a fully stirred reactor ($Pe_b = 0$) are shown in section b. We note especially the finite gradient for the $Pe_b = \infty$

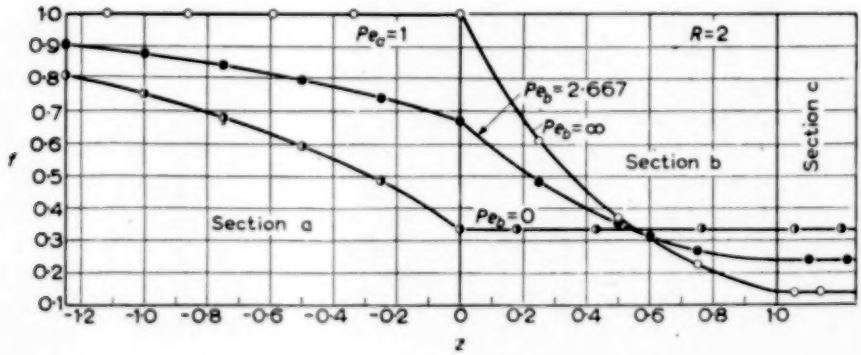

FIG. 4

curve at $z = 1$. For any finite diffusivity the gradient at that position becomes zero. The fore section (a) was arbitrarily assumed to have $Pe_a = 1$ in the illustration and the profiles as shown result. Because the Peclet groups were not taken with equal values between the sections the slopes are discontinuous at the boundary.

The HULBURT solution may be arrived at by normalization through division of the DANCKWERTS solution by $f(0)$. Although convenient for estimating relative importance of reaction and diffusion rates the solution is not consistent with the limit of a stirred reactor with infinite diffusivity in the reaction section.

APPENDIX*

Boundary conditions (11) and (13) are, in general, true for a three-dimensional and non-steady-state reactor since they contain terms which represent the only mechanisms considered for flow of reactant across a boundary.

When no diffusion occurs in the fore section ($Pe_a \to \infty$) boundary condition (11) becomes :

$$f(0-) = f(0+) - \frac{1}{Pe_b}\frac{df}{dz}(0+) \tag{26}$$

This equation holds during a time-varying change in f and the resulting discontinuity does not disappear in the steady state as evidenced by the present solution.

For boundary condition (13) :

$$f(1-) = f(1+)$$

and, as $Pe_c \to \infty$

$$\frac{df}{dz}(1-) \to 0 \tag{27}$$

in the nonsteady state if Pe_b is finite. This result may be shown as follows :

As $(Pe)_c \to \infty$, $\dfrac{\partial f(1+)}{\partial z} \to -\infty$ if $\dfrac{\partial f(1-)}{\partial z} < 0$.

This means physically, however, that section c acts on the surface $z = 1$ as a "sink," a result which is clearly absurd since no reaction takes place in section c. It follows therefore that as $(Pe)_c \to \infty$, $\dfrac{\partial f(1-)}{\partial z} = 0$ although, in general $\dfrac{\partial f(1+)}{\partial z} \neq 0$. Thus, even in the nonsteady state, no discontinuity will develop for any period of time at boundary (1). At the entrance boundary (0), however, the discontinuity is set up and maintained by the reaction and diffusion within the bed. If no diffusion occurs within the bed, no discontinuity will occur at the entrance boundary, (0).

It is to be noted that equation (27) is valid only for $Pe_c = \infty$ in the non-steady state, but for all values of Pe_c in the steady state. Also, Pe_b must be finite for equation (27) to be valid in either case.

*The generality of these equations and the two special cases were pointed out to the authors by Prof. ANDREAS ACRIVOS of the Department of Chemistry and Chemical Engineering, University of California, Berkeley 4, California.

NOTATION

a = a group, $(1 + 4R/Pe_b)^{1/2}$
A = cross-sectional area through which flow occurs.
D = diffusion constant in Fickian equation, molecular or turbulent.
f = fraction of reactant remaining
$f(0-)$ = composition at upstream side of fore section-reactor boundary
$f(0+)$ = composition at downstream side of fore section – reactor boundary
$f(1-)$ = composition at upstream side of reactor – after section boundary
$f(1+)$ = composition at downstream side of reactor – after section boundary
k = first-order reaction rate constant
L = reaction section bed length
N = constant in general solution for differential equation
Pe = Peclet group, Lu/D
R = reaction group, kL/u
u = linear velocity
z = dimensionless distance in the axial direction. Normalizing constant is L.

Subscripts

a refers to fore section
b refers to reaction section
c refers to after section

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Book reviews

Principles of Chemical Engineering Thermodynamics. Ernest D. Wilson and Harold C. Ries : McGraw-Hill, 1956. pp. ix. + 376. 56/6s.

The authors describe their book as being written for an undergraduate course in thermodynamics for chemical engineers. The contents include a discussion of the first and second laws, with applications to fluid flow, steam power plants, refrigeration, phase equilibrium and reaction equilibrium. Graphical representations of thermodynamic data are included, together with numerous useful illustrations in the text and about 120 problems for the student to solve for himself.

The first six chapters, which are concerned with properties of matter and the applications of the first law, are taken quite slowly and at a rather elementary level. The second law is thus not reached until almost half-way through the text. This results in a much faster pace in the second half and the last two chapters in particular are too highly condensed : phase equilibria, ideal and non-ideal solutions, reaction equilibrium and the third law, are all compressed into the space of 59 pages. These important topics are thus given a rather summary treatment.

The authors make very extensive use of the perfect gas law in the development of the theory and in their preface they remark that they believe this to be the best method of achieving simplicity of presentation. (And of course many other textbooks follow the same pattern.) Whilst admiring the simplicity which has been achieved, the reviewer feels that it is a mistaken policy in thermodynamics teaching to give undue prominence to perfect gases ; its effect is that students, having become habituated to the use of certain equations applicable only to perfect gases, blithely apply them to any type of substance, liquid, solid or gaseous. Thus students commonly write $dU = C_v\,dT$ and $dH = C_p\,dT$, as if these relations were applicable to a general change of state, which of course they are not. Occasionally the authors themselves seem to be led astray in a similar respect. Thus on p. 149-150 it is said that the equation

$$dS = \frac{C_p dT}{T} - \frac{R}{P}\,dP$$

is completely general and applicable to all systems.

Although there has thus been a tendency to oversimplify the theory, the book has some very good features and most of the writing is clear and straightforward. The reviewer enjoyed in particular the chapter on steam-power plants.

The problem of the presentation of thermodynamics is one of continual interest. On the one hand, the young engineer is usually much more interested in applications than in theory and therefore prefers a simplified approach; on the other hand, if he fails to achieve a real grasp of the fundamentals he is at a loss to know how to proceed when he is faced with unfamiliar problems, or when he should be making new and inventive applications on his own account. Thermodynamics, as we all know, is not an easy subject !

K. G. Denbigh

Thermodynamic Functions of Gases. Edited by F. Din, Butterworths Scientific Publications, 1956. Vol I 175 p. + vi, Vol. II, 201 p. + vi. 63s. each volume.

The publication of the first two volumes of this new series is a very welcome event. Their origin and purpose is described by Professor Newitt, in his preface, in the following words " The preparation of the surveys of the thermodynamic properties of gases described in these volumes has been undertaken in connection with a scheme sponsored by the Department of Scientific and Industrial Research in Great Britain. The work is organised by the Thermodynamics Committee of the Mechanical Engineering Research Board and is being shared among a number of academic and industrial organisations which have volunteered assistance. The purpose of this scheme is to provide reliable thermodynamic data for all industrially important gases, and now that the first eight surveys are ready, the Committee feels that they should be made generally available. Further surveys will follow in due course."

Each volume contains three or more sections, each dealing with a particular gas. Although these various sections have been prepared by different authors, they all follow a similar pattern, namely (1) survey of existing data, (2) construction of the temperature – entropy diagram, (3) discussion, (4) tabulation of the thermodynamic functions. The procedure agreed between the authors was thus to make a critical survey of the existing information and then from this data to construct the most reliable $T - S$ diagram, including the two-phase region, and finally to tabulate values of the entropy, enthalpy, specific heat and volume as functions of temperature and pressure.

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The difficult work of editorship has been very ably carried out by Dr. F. DIN and he also contributes a valuable critical discussion in the first volume on the methods of preparing thermodynamic diagrams and tables from experimental data. As he remarks, the engineer would be in a much better position to make the necessary allowances when using thermodynamic tables if he realized the approximations on which they are based. Tables for steam and other gases are certainly very far from revealed truth.

Thus, in this introductory section, Dr. DIN surveys the method of constructing the $T - S$ diagram by use of $P - V - T$ data, together with measurements of the heat capacity and the Joule-Thomson coefficient. The section is generally very lucid, but a few of the paragraphs left the reviewer not quite clear about the author's meaning.

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The remaining sections of the first volume, all carefully carried through as far as can be seen, deal with ammonia (P. DAVIES), carbon dioxide (D. M. NEWITT, M. U. PAI, N. R. KULOOR and J. A. W. HUGGILL) and carbon monoxide (SMEETON LEAH). The second volume comprises similar surveys on air (F. DIN), Acetylene (F. DIN), ethylene (W. F. L. DICK and A. G. M. HEDLEY), propane (N. R. KULOOR and D. M. NEWITT and J. S. BATEMAN) and argon (F. DIN).

Further surveys over another dozen or more gases are promised. The volumes will surely become an essential addition to any chemical engineering library.

KENNETH DENBIGH

F. H. KEATING : **Chromium-Nickel Austenitic Steels.** Butterworths Scientific Publications, London 1956. x + 138 pp. 25s. net.

THIS handbook on stainless steels is the outcome of the experience of long usage by the Imperial Chemical Industries of these materials. In order to ensure that each division of the company is fully informed on various subjects these handbooks were initiated for internal circulation about twenty years ago. They therefore presume text-book knowledge of the subject and are designed to bridge the gulf between text-books and practise. For stainless steels this is particularly valuable since, owing to the large variations in composition, it is very difficult for the user to make a fair assessment between the claims of various trade materials drawn to his attention by various makers.

The first chapter gives a 6 page introduction to the metallurgy of the subject and is followed by 22 pages on the historical development of the material. Chapter three has a small portion on manufacturing processes and a much larger section on various fabricating processes. Chapter four is 3 pages on castings.

The next two chapters on mechanical properties and corrosion are most valuable to the chemical engineer and discuss the strength of the materials up to 900°C and down to − 200°C. A guide is given to suitable maximum allowable working stresses for every 100°C from room temperature to 1,000°C. The situation regarding sub-zero temperatures however is still not very clearly cut.

A most useful table of the corrosion resistance of 18 : 8 steels stabilized with titanium or niobium is given for over 100 different chemicals and data is added for the effect of additions of molybdenum and copper.

A chapter on chemical analysis covers carbon, chronium, nickel, manganese, silicon, niobium, tungsten, molybdenum, sulphur, titanium and phosphorus.

The book should go a long way to secure that the next review of British Standards on these steels will (to quote the author's final words) 'provide simple documents to cover the purchases of British and foreign users' and not leave important matters of composition to be settled at the discretion of the manufacturer.

M. B. DONALD

Physikalisch-chemisches Rechnen in Wissenschaft und Technik. HANS FROMHERZ : Verlag Chemie, Weinheim, 1956. xii + 316 pp. DM 32·50 (£2 16s. 11d.)

IT is the author's intention in this book to give instructions for the use of physical chemistry in science and technology. A large part (206 pages) of some fourteen chapters, is devoted to worked-out problems which, in each chapter, are preceded by a summary of the formulae to be used. The gas laws, solutions, vapour pressure, thermochemistry, chemical equilibrium, electrochemistry, and reaction kinetics are discussed. Naturally, the author has had to confine himself to a selection from the wide range of subjects existing in this field. The choice is on the whole a good one, but a few criticisms may be made.

The discussion of the problems of true gases (Chapter III), where only the van der Waals equation is dealt with, should have been supplemented by generalized state diagrams (particularly in view of their successful application in the petroleum industry).

In the questions about the determination of molecular weights in solutions, etc. (Chapter VII) the activity coefficients of the solvent and the solute are not taken into consideration, with the result that the determinations only apply to strongly diluted solutions. Some problems about the determination of activity coefficients would not have been out of place in this chapter.

The excellent Antoine equation could have been mentioned in connection with temperature dependence of vapour pressure (Chapter VIII).

The chapters on thermochemistry and position of equilibrium (Chapters IX, X, XI) are very well handled. In these chapters the author should have drawn attention of his readers to the existence of the excellent modern American tables which give a good summary of a large part of the available thermodynamic quantities.

The last three chapters deal with electrochemistry and the reaction kinetics, and in them a good selection of problems is given.

A good symbol and subject index as well as some tables with fundamental quantities and conversion factors terminate the book.

The foregoing remarks, which partly arise from a personal preference, are not meant in any way to disparage the high quality of this well-presented book. This work can thus be recommended without reservation to chemists and chemical engineers, and especially to students of the subjects. This reviewer has enjoyed reading the book.

H. A. G. Chermin

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